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THE CHEMISTRY OF ANÆSTHETICS.*

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SACRED, profane and mythological literature abound in incident, fact and fancy, showing that from earliest times man has sought to assuage grief and pain by some means of dulling consciousness. Recourse was had to the inhalation of fumes from various substances, weird incantations, applications of drugs, both external and internal, pressure upon important nerves and blood-vessels, and the laying on of hands, or animal magnetism. Each has played its part in the mitigation of human ills. It was not until the close of the eighteenth century, however, that modern surgical anæsthesia was foreshadowed. Then it was that the discovery of hydrogen, nitrogen, oxygen, and nitrous oxide—pneumatic chemistry, as it were—created a field of pneumatic medicine. In 1798, the Pneumatic Institute was founded for the purpose of investigating the "medical powers of factitious airs or gases" and was set up at Clifton by Dr. Thomas Beddoes. The immediate idea to be followed out was the treatment of phthisis and other lung troubles by inhalation of various gases. Humphrey Davy was assigned the office of superintending the experi-

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ments. One of the first outcomes of his researches, the result of his experimentation with nitrous oxide upon animals, is given in the following historical and often quoted sentence[1]:

"As nitrous oxide in its extensive operation appears capable of destroying physical pain, it may probably be used to advantage during surgical operations in which no great effusion of blood takes place." Davy actually inhaled the gas, and recorded his own sensations and the behavior of others after they had inhaled it.

In 1805 Dr. Warren, of Boston, used "sulphuric ether" on a patient suffering with phthisis, and the year following it was used in attacks of asthma; but Faraday in 1818 was the first to recognize its value as an anæsthetic.

Chloroform was discovered in 1831 independently by Liebig, Soubeiran and Guthrie. It is reported in the *American Journal of Science* for January, 1832, that Dr. Ives, of New Haven, used chloroform in surgery.

In 1828, Girardin read a paper describing surgical anæsthesia by means of inhaled gases; but the honor of the discovery of surgical anæsthesia has been claimed, with more or less acrimonious partizanship, for four others, namely, Long, of Jefferson, Ga., who anæsthetized a patient with ether in 1841; Wells, of Hartford, Conn., who used nitrous oxide in dentistry in 1844; and Morton, a pupil of Wells, used ether instead, at the suggestion of Jackson, a chemist, who later claimed to be the real discoverer. Simpson, in 1847, first used ether in midwifery and later he employed chloroform, whose anæsthetic properties had been previously described by Flourens. In 1868 Andrews, of Chicago, called attention to the use of oxygen with nitrous oxide to produce a non-asphyxial form of anæsthesia. In 1906, Brown, of Cleveland, used a warmed mixture of nitrous oxide and oxygen, followed by ether and chloroform, with great success. In 1909, Gwathmey, of New York, moistened the gases.

I need not recount the historical data which have to do with other anæsthetics, a list of which I have published in the *American Druggist*, and my remarks this evening will therefore be limited to nitrous oxide, ether and chloroform; and these

[1] Davy "Researches, Chemical and Philosophical, chiefly concerning Nitrous Oxide," London, 1800.

few facts—the results obtained from careful unbiased investigation of the literature and other forms of evidence—are given without elaboration or argument.

The writer knows of no satisfactory basis of classification of anæsthetics. Some are general, others local, but the latter may become general in their effects, depending upon conditions. Hence, they will be considered in chronological order.

NITROUS OXIDE.

In 1772, Priestley first prepared nitrous oxide by reducing NO with moist iron filings. In 1793, Deiman and others prepared the gas by heating NH_4NO_3, essentially the commercial process for its manufacture to-day. It is usually carried out by heating mixed salts, as $NaNO_3$ and $(NH_4)_2SO_4$, $NaNO_3$ and NH_4Cl, etc.[2]

Commercial nitrous oxide is apt to contain these impurities: Cl_2, NO, NO_2, HNO_3, NH_3, HCl, CO_2, O_2, N_2, and the rare gases of the air. It is usually purified by passage through solutions of sodium hydroxide, ferrous sulphate, and sulphuric acid. Further purification may be accomplished by the formation of a hydrate [3] below 0° C. and heating this hydrate ($N_2O,6H_2O$)—that is, by fractional condensation [4] and by fractional distillation.

The following impurities may be suspected in a cylinder of compressed nitrous oxide:

1. Solids.
2. Liquids.
3. Gases and vapors:

H_2O,
halogen acids, HNO_3, organic acids,
O_3, NO_2, N_2O_3, SO_2,
NH_3, organic bases,
CO_2, halogens, oxides of chlorine,
HCN, $(CN)_2$,
PH_3, SbH_3, AsH_3, H_2S,
O_2, H_2,
CO, CH_4, organic matter (from valve lubricants),
N_2, rare gases of the air.

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[2] Baskerville and Stevenson, *J. Ind. and Eng. Chem.*, iii, No. 8.
[3] Villard, *Compt. rend.* (1894), cxviii, 1096.
[4] Stolzenberg, *Ber.*, xliii, 1708.

For these impurities, a qualitative search should first be made and then, whenever necessary, a quantitative determination. A systematic procedure has been devised, a detailed account of which on this occasion would be unwelcome. Those substances known to be irritant to the respiratory organs should be tested for to make sure of their absence before the gas is used in surgical cases. It may be said that established manufacturers appreciate this and govern themselves accordingly, consequently it is not necessary to test every cylinder supplied by them. Their integrity constitutes an asset—a fact which, unfortunately, is not the case with all manufacturers of all drugs.

Beyond the absence of disturbing impurities, the improved methods of the use of nitrous oxide for anæsthetic purposes de-

TABLE I.

ANALYSIS.

No.	N_2O	H_2O	CO_2	NH_3	O_2	N_2, etc. by diff.	N_2O by explosion	N_2O by $Cu + CO_2 + H_2$	N_2O by $Cu + H_2$
1	99.7	0.13	0	0.006	present	0.16	97.5	99.4	99.7
2	96.6	0.15	0	0.001	present	3.25	95.0	96.2	96.0
3	99.5	0.15	0	0	present	0.35	97.3	99.5	99.5
4	95.9	0.16	present	0	present	3.94	94.1	95.6	95.9

mand a knowledge of the approximate content of nitrous oxide in the commercial product, as will become apparent later; hence a method for its determination is desirable. Various methods have been proposed—for instance, decomposition into N_2 and O_2, burning with hydrogen, explosion with hydrogen, combustion of charcoal with absorption of CO_2 produced, explosion with CO, oxidation of a fused mixture of sodium carbonate and Cr_2O_3 and determining the amount of Na_2CrO_4 produced, and absorption in alcohol; and none is satisfactory. Dr. Stevenson and the writer have devised a new method, which gives accurate results in hands skilled in the manipulation of gases. It depends upon passing a definite quantity of the gas over heated copper gauze, after a preliminary treatment to remove oxygen or compounds which produce copper oxide from the sample, and then passing hydrogen through the apparatus, and absorbing the water formed.

Table I, which is self-explanatory, exhibits the results of our analyses of compressed nitrous oxide as supplied by American manufacturers.

Nitrous oxide which is to be used for anæsthesia, should contain at least 95 per cent. of N_2O and no solids, liquids, combustible organic matter, chlorine, or other oxides of nitrogen. A small amount of carbon dioxide, according to the investigations of Gatch, can have no evil effects. If present, however, the percentage should be known.

ETHYL ETHER.

Experiences of expert anæsthetizers, often not accounted for by idiosyncrasy, obtained in the use of ethyl ethers supplied by various manufacturers in numerous surgical cases, furnished the motive for this phase of the investigation of the chemistry of anæsthetics. The standards laid down by the various pharmacopœias of the world are not uniform. In view of that fact alone, a thorough investigation seemed called for. Enquiries addressed to large consumers of the solvent in manufacturing processes adduced further need for satisfactory methods of determining the purity of ethyl ether and of detecting impurities introduced, or proving their absence if eliminated, in the modification of raw products used in its manufacture. The presence of small amounts of substances has oftentimes been the cause of a chemical reaction proceeding in a particular direction by virtue of a "catalytic action." So the presence of even traces of certain substances, as peroxidized compounds, aldehyde, etc., may have caused some reactions to be incorrectly explained, or to follow an unusual, or unaccounted for, route.

Ethyl ether is still made commercially by the historical process of treating alcohol with sulphuric acid—hence the misnomer of "sulphuric ether," or "vitriolic ether"—although other synthetic processes have been proposed, some of which have been tried out, but always without commercial success.

In this connection reference may be made to the method devised by Fritsche for the preparation of ether free from alcohol. In this method gas containing ethylene is treated with sulphuric acid,[5] and the ethyl-sulphuric acid so obtained is con-

[5] *Z. anal. Chem.*, xxxvi, 298; U. S. Patent No. 475,640, Jan. 19, 1897.

verted into ether and sulphuric acid by means of water. It was reported that this process was operated on a commercial scale in this country for some time, but that the industry was destroyed by the Denatured Alcohol Act.[6] It is likely, however, that a similar industry may be revived, as natural gas might serve as a suitable material from which to prepare ether.[7]

The quality of ethers on the market depend upon, first, the purity or grade of the alcohol used; and, second, secondary reactions which take place, not only with impurities in the alcohol, but with ethyl hydroxide itself. For example, ethyl ether made from ethyl alcohol denaturized by methyl alcohol contained other ethers, as dimethyl oxide or methyl-ethyl ether, not found in the ether made from the old rectified spirit. The generous interpretation of the denatured alcohol act by our Government officials, whereby alcohol denaturized by ether itself may now be used, eliminated these substances. Many of the impurities traceable not only to the quality of the raw products used, but the secondary reactions of their virgin impurities, due to variations, as in temperature, pressure, and other conditions, were removable and have in a large measure been removed, or much reduced, by subsequent purification.

It was found necessary in our work to make discriminations in the various grades of ether,[8] so the following classification was settled upon and its adoption by others is suggested:

1. *Pure Ether.*—Absolute ether—ether free from all impurities.

2. *Anhydrous Ether.*—Ether free from water, but which may contain traces of ethyl alcohol and acetaldehyde.

3. *Anæsthetic Ether.*—Ether complying with the pharmacopœial requirements. Such ether may contain ethyl alcohol (up to 4 per cent.), and traces of acetaldehyde, acids, and water, although in the opinion of the author, it is highly desirable that the three last mentioned,—*i.e.*, the impurities,—be totally eliminated.

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[6] *Bull. 92*, U. S. Dept. of Commerce and Labor, Bureau of the Census, 1909, p. 96.

[7] Cf. French Patent 352,687, of 1905, of Lance and Elworthy.

[8] Chas. Baskerville and W. A. Hamor, *J. Ind. and Eng. Chem.*, iii, 301, 378.

4. *Commercial Ether.*—Ether which contains at least 95 per cent. by weight of ethyl oxide.

All other grades of ethyl ether should be classed as *Impure Commercial Ether.*

The standard of purity for laboratory ether, or ether for analytical purposes, is entirely dependent upon the purpose for which it is intended. For ordinary reagent purposes, the grade specified under *Anæsthetic Ether* is suitable, and in general may be said to answer all such purposes; but in special cases the other ethers may be employed. Our attention will be confined to anæsthetic ether.

The specific gravity of ether intended for anæsthesia should not exceed 0.720 at 15° C., providing an ether containing minimum quantities of alcohol and moisture is required; however, an ether which shows a specific gravity of 0.7215 (2 per cent. absolute alcohol), 0.7228 (3 per cent. absolute alcohol) or even 0.724 (4 per cent. absolute alcohol), providing the sole "impurity" is ethyl alcohol, is acceptable for anæsthetic purposes according to various pharmacopœias.

In this connection it may be stated that for various reasons a pure ether may be diluted with ethyl alcohol when it is to be used for anæsthesia. Impurities then observed may be due in part to the alcohol used in dilution. Practically all ethyl alcohol contains some acetaldehyde.

Ethyl alcohol serves, it is asserted, as a preservative for ether when the latter is properly stored; and small amounts interfere in no way with the application of ether in anæsthesia. However, the presence of alcohol is unnecessary except when ether is administered by the "drop method." In this case, the presence of alcohol prevents too rapid volatilization and consequent chilling of the apparatus with which the ether is administered. Some have maintained that pure ethyl ether is unsuitable for anæsthesia, but it is a fact that the vapor from ether containing alcohol, when passed through water at 40° C., whereby the alcohol is removed, may be and is being used now with great success for anæsthesia. The presence of excess moisture in liquid ether should be guarded against, since ether in contact with water, or moist air, in time gives rise to various impurities of an objectionable nature. Thus anæsthetic ether even of proper grade may develop impurities to be avoided quite as

much as if they had been introduced in the original materials or later produced in the manufacture or added in the preparation for distribution in commerce.

Instances of sophistication have been known, but now they are comparatively rare. There are more frequent instances of contamination resulting either from the lack of control in the manufacture or from careless storage. It is almost needless to call attention to the necessity for having a substance such as anæsthetic ether, which is used so extensively in the most critical cases, as pure as human ingenuity can provide it.

Traub pointed out that a sample of "impure" ether usually leaves a fruity odor when allowed to evaporate on filter paper, and it is generally recognized that filter paper which has been moistened with ether must possess no odor after the evaporation of the ether. This test is given in the pharmacopœias of Austria, Belgium, Japan, Switzerland, Spain, Great Britain, Germany, and the United States. Generally a positive result may be said to be indicative of the presence of "heavy oil of wine," amyl, propyl, or butyl compounds, or fusel oil. These materials, if present, may excite coughing during inhalation. The occurrence of fusel oil and of "heavy oil of wine" is rare in the case of anæsthetic ethers and they are really only likely to occur in commercial and impure commercial ethers.

Ether, when freshly distilled over sodium, possesses a specific gravity of 0.7178 to 0.719 at 15/4° C.; but if it is not, immediately after its rectification, drawn off into vessels, which are sealed at once and carefuly stored, the specific gravity increases in a short time. The purest ether procurable on the market is of 0.718–0.719 specific gravity at 15°, but this absorbs water on exposure to the atmosphere, and rises to 0.720–0.721 specific gravity, when it becomes fairly constant.

Since the specific gravity of ether is 0.7178 to 0.719 at 15° C., those requiring ether of 0.720 specific gravity thus allow minimum amounts of water and alcohol. Unless the ether is dried carefully by means of sodium, for example, and is kept constantly dehydrated by storing over such an agent, or great care is taken in storing it after final rectification, it is practically impossible to maintain the specific gravity originally possessed by the ether.

The ethers recognized as official by the pharmacopœias of various countries possess the specific gravities shown in Table II.

Although the boiling point of pure ether is + 34.6° at 760 mm., there are no ethers of anæsthetic grade on the market which comply fully with this requirement, owing to the mutually opposing influences of water and alcohol on the boiling point, and only ether distilled over sodium closely approximates it. Since, therefore, these influences render the constancy of the boiling point as ordinarily determined of little or no use as a criterion

TABLE II.

Specific gravity.	Countries where recognized.
0.716–0.717	United States.
0.720	Russia; Great Britain; Mexico; Spain; Japan; Germany; France; Belgium; Sweden; Holland; Hungary.
0.720–0.722	Switzerland; Italy; Norway; Denmark.
0.725	Austria.
0.724–0.728	Finland.
0.728	Portugal.

of purity, it is sufficient to require that ether shall commence to distil at a temperature not under + 34° C., and that it shall possess a boiling point of + 34° to 36° C. We have found that ether purified by distillation over sodium yields a distillate amounting on the average to 99.50 per cent. of the total amount taken when fractioned, this percentage distilling off between + 34° to 35° C.; whereas three ethers used for anæsthesia gave the results shown in Table III.

TABLE III.

Temperature.	Percentage by volume.		
	I.	II.	III.
25°–34°	1.00	1.00	1.00
34°–36°	98.50	97.00	97.50
36°–37°	0.50	2.00	1.50
37°–42°	....	....	....

In view of these facts, augmented by other experiments, the writer is of the opinion that ether intended for anæsthetic purposes should, when carefully fractionated, yield a distillate amounting to at least 97 per cent. by volume between + 34° and + 36° C., and that not more than 1 per cent. should distil off below + 34° C., if it is to comply with present pharmacopœial requirements.

Ethers recognized as official by various countries possess the boiling points shown in Table IV.

The writer, assisted by Mr. W. A. Hamor, has conducted an extensive investigation of the changes which occur in ethyl ether during storage, and the experimental data obtained lead to the conclusion that the oxidation of ether in the presence of moisture is productive of a series of complex conversions, initiated, however, by the formation of hydrogen dioxide. The slow combustion of pure ether in the presence of water, and under such conditions as exist when it is improperly stored, would appear to occur in the following stages:

1. The formation of hydrogen dioxide from water and oxygen of the air. This is particularly likely in cases where there

TABLE IV.

Boiling point.	Where recognized.
34.5°	Great Britain.
34°–36°	Finland; Austria.
35°	Hungary; Japan; Germany; Belgium; Russia.
35.5°	United States.
35°–36°	Switzerland.
36°	Italy; Norway; Denmark; Portugal; Holland.
36.5°	France.

is direct exposure to light, and it is more or less activated by contact action.

2. Dissociation of hydrogen dioxide into water and oxygen, which latter then exerts a direct oxidizing action, resulting in the formation of the following: acetic peroxide; acetaldehyde and acetaldehyde peroxide; and eventually acetic acid. The formation of acetic peroxide would facilitate a series of oxidations, and by its hydrolysis alone, acetic and peracetic acids would be formed. The peracetic acid would then become converted into acetic acid and hydrogen dioxide; therefore, it is reasonable to conclude that a continuous cycle of changes occurs in the ether during its oxidation and that such changes result in the simultaneous formation and occurrence of peroxidized compounds, intermediate (aldehyde) and ultimate (acetic acid) resultants.

When anhydrous ether is exposed to the action of atmospheric oxygen during improper storage, there is every reason for the conclusion that peroxidation occurs; such action is similar to that which takes place when anhydrous ether is ozonized, but

the process is much less active, being indirect. During storage under conditions which would be conducive to oxidation, the absolute exclusion of moisture is not attained. Changes occur similar to those which ensue in the presence of water, but of a much slower and much less intense nature.

Our experimental work seems to establish beyond any doubt the fact that ether of anæsthetic grade contains peroxidized compounds after exposure to varying temperature conditions and sunlight, in the presence of atmospheric oxygen, for considerable periods of time, especially when it is stored in colorless glass vessels, or in badly stoppered tin containers.

Acetaldehyde, the presence of which may account for some of the observations made in practice, is one of the impurities most likely to be generated by exposing partially filled containers to varying atmospheric conditions for continued periods of time. Ether should not be stored in glass vessels for any length of time without being tested for oxidation products before use; and the tin containers should be of such capacity that they need not be opened without being emptied when the ether is employed for anæsthetic purposes. The sealing of tin containers will be referred to later.

With regard to the acidity of the various anæsthetic ethers on the American market, it may be said that none that we have examined contained acids (sulphurous, sulphuric, acetic) in what may be termed injurious amounts, since the amount present never exceeded 0.002 Gm. of acetic acid per 100 c.c. of the sample in any case. The degree of acidity is liable to vary more or less in both directions in short intervals during storage in glass vessels, just as in the case of the oxidation of ether itself. The variations in acidity—theoretical, but not sensible in general—may be due to differences between the rapidity of the oxidation and the saturation of the acids by the bases of the glass. In fact, it should be mentioned here that the nature of the ether container is of vast importance in the light of the oxidation changes which are possible. The extent of the oxidation—or, for that matter, any oxidation at all—is dependent upon the quality of the glass used in bottles for storing ether; and in the case of metallic containers, in view of some recent researches, it is probable that all metals which show anomalous anodic conductivity are likely to develop free hydrogen dioxide in contact with water

and oxygen. The presence of such metals should, therefore, be guarded against.

Since it is highly important that ether intended for anæsthetic purposes should be carefully manufactured and properly stored, as prolonged exposure to light and air greatly affect the results of etherization, causing coughing, suffocation, and even dangerous after-effects, such ether should always be tested for peroxides and aldehyde, and the presence of the latter should be rigorously guarded against, or the ether, if so contaminated, should be administered by a method which eliminates these impurities before it is introduced into the animal system.

We have made an examination as to the value of all proposed tests for the impurities in ethyl ether and devised several new and superior ones. A scheme for examination has been worked out and is now available in the literature.[9]

CHLOROFORM.

Liebig prepared chloroform from chloral. Soubeiran treated alcohol with "bleaching powder." Schering generated his "bleach" in the presence of alcohol by electrolysis. Then "methylated spirit" was used, whereby so-called "methylated chloroform" was obtained. Liebig also obtained chloroform by the action of "chloride of lime" upon acetone. Böttger and others used acetates (1848), and then chlorine was liberated in acetone by electrolysis. This process is used extensively in this country now. Methane of natural gas has been burned in chlorine, but this process has not proved successful commercially so far, although "gas chloroform" is spoken of by some in a wise way. Carbon tetrachloride, made by chlorinating carbon disulphide, is being reduced by the process of Smith to produce much chloroform in this country at present. "Chloral Chloroform" is imported in small quantities.

From the variety of "ausgangs-material" and different methods used, it is quite evident that crude chloroform may contain a wide range of impurities, which may vary not only with the materials used, but the conditions of manufacture. Alcohol has been removed from chloroform by washing with water, the chloroform being subsequently dried over calcium

[9] *J. Ind. and Eng. Chem.* iii, 395.

chloride. Potassium hydroxide has been used to remove excess chlorine and acids. Manganese dioxide has been used to remove sulphur dioxide. Chloroform has been treated with concentrated sulphuric acid until the acid was no longer colored, and then the vapors of chloroform have been passed through towers of crystallized sodium carbonate; rectification has followed. To remove special impurities or decomposition products of the chloroform itself, chloroform has been treated with lead dioxide; with potassium permanganate, or with dilute sodium thiosulphate; or it has been distilled over 2 per cent. paraffin or poppy oil.

"Chloroform Anschütz" is obtained by distilling from crystals of salicylid-chloroform ($C_{28}H_{16}O_8.2CHCl_3$). "Chloroform Pictet" is made by chilling chloroform to — 80° C., filtering off the solids produced, and then lowering the temperature to — 82° C. and drawing off the liquid impurities. The frozen chloroform is then fractioned, the intermediate 80 per cent. of the distillate being taken.

TABLE V.

DETERMINATIONS OF THE SPECIFIC GRAVITY OF CHLOROFORM.

0°	1.52523, 1.52657
11.8°	1.5039
12°	1.496, 1.512
15°	1.485, 1.4946, 1.4905, 1.4976, 1.5066, 1.5107, 1.4989, 1.4980, 1.500, 1.50027, 1.50085, 1.49887 (Baskerville and Hamor).
15.5°	1.500
16.5°	1.472
17°	1.491, 1.507
18°	1.48
18.58°	1.48978
25°	1.48432, 1.48492
29°	1.49089
35.86°	1.45695
60.8°	1.4081
61.2°	1.40877
63°	1.3954, 1.4018, 1.408114

The specific gravity values of chloroform have been determined by different workers [10] as shown in Table V.

In the course an investigation of the decomposition of chloroform, we prepared pure chloroform. This possessed a density of 1.49887 at 15/4° C. (average of six determinations), a result in close agreement with the values of Thorpe and

[10] Chas. Baskerville and W. A. Hamor, *J. Ind. and Eng. Chem.*, iii.

Timmermans. This value may be taken as the correct specific gravity at the temperature noted.

The anæsthetic chloroform on the American market varies in specific gravity from 1.4730 to 1.4827 at 25/25°, usually in close proximity to 1.476, the minimum density permitted by the *Pharmacopœia*. The samples of chloroform of German manufacture examined varied in specific gravity from 1.487 to 1.492 at 15/15°, although one sample possessed a density of 1.497 at this temperature. Since the correct specific gravity of chloroform is 1.49887 at 15/4°, those officials requiring chloroform of lower density—that is, anæsthetic chloroform—allow the addition of alcohol, and consequently the presence of small amounts of water; the permissible addition usually varies from 0.25 to 1 per cent.

Specific gravity determinations are not to be regarded as criteria of purity beyond indicating the amount of alcohol in chloroform.

The chloroform constants according to various editions of the United States *Pharmacopœia* are as follows:

Date.	Density at 15°	Boiling point.
1851	1.49	142° F.
1869	1.490–1.494	140° F.
1873	1.480	142° F.
1882	1.485–1.490	60–61° C.
1893	Not below 1.490	60–61° C.

The specific gravities of the chloroform recognized as official by the pharmacopœias of various countries are given in Table VI.

The boiling points of anæsthetic chloroform recognized as official by the various pharmacopœias are shown in Table VIII.

In general, it may be said that no specific directions are given in the pharmacopœias for the determination of the boiling point and the influence of the variables (alcohol and water in particular) has not received enough attention.[8] Opinions are divided as to the value of the determination as a criterion of the purity of anæsthetic chloroform. In the writer's opinion, it is of no value without a knowledge of the content of alcohol and water. In making a careful fractionation of 500 Gm. of anæsthetic chloroform made from acetone, containing 0.5 per cent. alcohol and 0.026 per cent. water, but otherwise pure, the temperature

TABLE VI.

DENSITIES ACCORDING TO VARIOUS PHARMACOPŒIAS.

1.480 ..... Spain; Portugal; Mexico.
1.489 ..... Switzerland.
1.490 ..... Greece.
1.497 ..... Chili.
1.498 ..... France.
1.500 ..... Romania.
1.485–1.489 ..... Germany; Denmark, Hungary; Norway; Sweden; Finland.
1.485–1.490 ..... Belgium.
1.485–1.495 ..... Japan.
1.485–1.500 ..... Austria.
1.490–1.495 ..... Italy.
1.490–1.495 ..... Great Britain.
1.498–1.500 ..... Holland.
1.490–1.500 ..... Russia.
Not below 1.476 at
25° ..... United States.

TABLE VII.

BOILING POINTS OF CHLOROFORM DETERMINED BY DIFFERENT SAVANTS.

Year.	Observer.	Temperature.
1883	Schiff	60.9° at 754.3 mm.
1884	Perkin	62.0° at 760 mm.
1885	Bauer	61.0° at 760 mm.
1899	Thayer	61.6° at 760 mm. 61.64° at 760 mm.
1899	Pettit	61.97° at 760 mm.
1904	Wade and Finnemore	61.15° at 760 mm.
1911	The Author	61.20° at 760 mm.

TABLE VIII.

CHLOROFORM BOILING POINTS ACCORDING TO VARIOUS PHARMACOPŒIAS.

59.5–61.5° ..... Sweden.
60° ..... Italy.
60.8° ..... Spain; France: Chili; Romania.
61° ..... Mexico; Greece.
60°–61° ..... United States; Russia.
60°–62° ..... Great Britain; Germany; Austria; Switzerland; Belgium; Denmark; Norway; Japan; Finland.
61.3° ..... Holland.
61°–62° ..... Hungary.

rose at once to + 55.5° C., at which point part of the alcohol and water with some chloroform passed over, the remainder going over between + 59.4° and + 61°. The following fractions were obtained:

Temperatures.	Weight of fraction.
55.5–59.4°	10 Gm.
59.4–61.0°	177 Gm.
61.0–61.2°	300 Gm.
Above 61.2°	13 Gm.

The influence of alcohol and water, separately or together, on the boiling point of chloroform, may be seen from Table IX.

There has been not a little diversity of opinion among chemists as to the nature and products of the decomposition of chloroform, especially the changes which chloroform undergoes upon exposure to air; in fact, this discordance dates from the introduction of chloroform as an anæsthetic and prevails to-day. This condition is ascribable to the many influencing factors occasioned by the degree of purity of the chloroform under examination, the

TABLE IX.

BOILING POINTS OF MIXTURES OF CHLOROFORM, ALCOHOL AND WATER.

Constituents.	Per cent. chloroform.	Boiling point.
1. Chloroform-alcohol-water	92.5	55.5°
2. Chloroform-water	97.5	56.1°
3. Chloroform-alcohol	93.0	59.4°
4. Chloroform	100.0	61.20°
5. Alcohol-water (95.5 per cent. alcohol)		78.15°
6. Alcohol		78.3°
7. Water		100.00°

extent and nature of the exposure; but is principally due to the failure to consider, and therefrom to correctly interpret, the rôle of the general variable, alcohol, and with it the accompanying moisture.

The products of the decomposition of "pure" chloroform, according to various investigators, may be thus summarized:

Chlorine; hydrochloric acid: Morson; Maisch; and Hager.

Carbonyl chloride: Rump; Regnault.

Carbonyl chloride; hydrochloric acid: Stark; Ramsay; Schoorl and Van den Berg; and Dott.

Carbonyl chloride; chlorine: Brown; Schacht and Biltz; and Adrian.

The formation of carbonyl chloride is alone definitely agreed upon.

The decomposition of chloroform has been universally conceded to be an oxidation process. It is generally accepted that chloroform is unaffected by light alone, and that light, although it accelerates oxidation, is not a necessary factor in the process (Hager; Rump; Brown; Schoorl and Van den Berg); however, several investigators appear to have inclined to the view that light favors decomposition (Regnault; Dott).

With regard to the changes which occur in anæsthetic chloroform during exposure to air and light, there also exists a decided diversity of opinion, principally owing to the fact that no examinations were made during the course of the various investigations, so far as we are aware, for the presence of the oxidation products of alcohol in such chloroform. The whole subject required investigation, and accordingly an experimental study of the decomposition of both pure and anæsthetic chloroform was carried out. It was also hoped to throw light on, if not fully explain, the rôle of alcohol[11] and other substances in the so-called preservation of chloroform, a satisfactory explanation of which has been wanting.

Various samples, some twenty-three in all, of both pure chloroform[12] and chloroform containing the usual pharmacopœial amounts of alcohol and water, were exposed, in well-stoppered[13] containers of various sizes, and containing varying amounts of the samples, and of both colorless and anactinic glass, such as are customarily used in the trade, for different

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[11] The amounts of alcohol stated as permissible in the various official chloroforms intended for anæsthetic purposes are as follows:

Belgium	1.0 per cent.
Denmark	1.0 per cent.
Sweden	0.5–1.0 per cent.
United States	0.6–1.0 per cent.
France	0.005 part by weight.
Italy	0.5 per cent.
Switzerland	1.0 per cent. absolute.

[12] This chloroform was prepared according to the method of the authors, and was absolutely pure.

[13] No cork stoppers unprotected by metal caps were employed. In the experiments on pure chloroform, glass-stoppered bottles were solely used.

periods of time, but at room temperature (20° C.), from September to May, inside of a window having direct southern exposure. The conditions were extreme, but nevertheless were similar to those obtaining in many pharmacies and hospitals.

The anæsthetic chloroform used was examined prior to the experiments, and only such chloroform as was found to be free from all impurities was used. However, an amount of water equivalent, on the average, to 5.1 per cent. by volume of the alcohol present was permitted.[14] Thus each sample was of pharmacopœial grade.

The tests applied for the detection of the oxidation products of chloroform and alcohol were those previously proved out in our work. Quantitative determinations of the impurities developed were made when possible.

The experimental results warranted the following conclusions:

1. The products of the oxidation of *pure* chloróform are carbonyl chloride and hydrochloric acid, which come about according to the reactions:

$$CHCl_3 + H_2O + O_2 = COCl_2 + HCl + H_2O_2;$$
$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O.$$

We are convinced that oxidation will not occur if water be excluded, and the absolute exclusion of moisture appears to be impossible in practice. Hydrogen dioxide is formed, although we have been unable to detect it in chloroform undergoing oxidation and therefore conclude that its existence is ephemeral, and oxidation of the chloroform continues throughout the period of the exposure. The rôle of the water is that of a true chemical catalyst. The decomposition of pure chloroform is accelerated by light, as was shown by a comparison of the results obtained in the experiments wherein colorless glass was used with those in which anactinic glass containers were employed. Carbonyl chloride is formed with increased readiness in the presence of acids.[15]

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[14] The alcohol content of the anæsthetic chloroform used was determined quantitatively by the method of Nicloux.

[15] Cf. Lowry and Magson, *Trans. Chem. Soc.*, xciii, 121, who observed that the formation of carbonyl chloride is evidently accelerated by the presence of acids.

The extent of the oxidation is dependent upon the nature of the container, the amount of air present, the purity of the sample, and the intensity of the light to which it is exposed. With light alone, when no air is present, no decomposition occurs for ordinary periods of exposure; and in cases where there is air contact alone, and no exposure to light, the oxidation is slow.

Free chlorine can only result from the photochemical decomposition of carbonyl chloride.[16]

$$COCl_2 \rightleftarrows CO + Cl_2.$$

It is likely that in the cases where "chlorine" was identified as an indication of incipient alteration of chloroform, hydrogen dioxide was the cause of the reactions observed. No chlorine was found when containers of anactinic glass were used; and when chlorine is detected, it must be the result of a secondary reaction.

2. The products of the oxidation of *anæsthetic* chloroform are primarily the oxidation products of alcohol, and no decomposition of chloroform itself occurs while the oxidation of alcohol proceeds. When the oxidation of alcohol reaches a maximum, decomposition of the chloroform goes on as in the case of pure chloroform, with the exception that chlorinated derivatives of the oxidation products of alcohol may result. The decomposition of the chloroform itself is retarded, even prevented, so long as oxidation of the alcohol proceeds, and the retardation is consequently dependent upon the amount of alcohol present. The extent of the oxidation is subject to the conditions referred to in the oxidation of pure chloroform. It is important to note, however, that anæsthetic chloroform always contains water, the usual amount being about 0.05 per cent. by volume, according to our experiences.

At the inception of this investigation, it was considered possible that the instability of chloroform of all grades might be due to the presence of some catalytic agent, the removal of which would lead to beneficial results, as has been found in the case

[16] Coehn and Becker, *Ber.*, xliii, 130; and Weigert, *Ann. Physik.*, (4), xxiv, 55. The influence of light on the reversible reaction, $CO + Cl_2 \rightleftarrows COCl_2$, is purely catalytic.

of sodium hypochlorite,[17] for example. We have arrived at the conclusion that, given proper purification, the chloroform prepared from chloral hydrate, alcohol, acetone, or carbon tetrachloride, is in all cases identical from an anæsthetic point of view and in decomposition products, as we know they are identical in chemical composition. But it was ascertained that the oxidation of alcohol is accelerated by the presence of oxidizable bodies in solution and that foreign organic substances have a detrimental influence upon chloroform—which shows the necessity of having anæsthetic chloroform of a high degree of purity, from whatever source it may be prepared.

This leads to the rôle played by ethyl alcohol in the preservation of chloroform, for alcohol does prevent the decomposition of chloroform, as first suggested by Squibb, in 1857, and later (1863) by Brown, independently.

Those who have investigated the part played by alcohol in preserving chloroform up to the present time have held that either chloroform decomposes in the presence of alcohol and that the alcohol takes care of the decomposition products, or the alcohol acts as a "catalytic retarding agent" (Stadlmayr).

The preservative action of alcohol is due to the combination of the retarder with certain of the reacting substances; and any substance soluble in chloroform and readily oxidizable will exert an inhibitory effect on the oxidation of chloroform itself, for example, sulphur and many other substances.[18] All compounds which have been found to serve as preservatives of chloroform are reducing agents, and the effect is only due to their capacity for oxidation. In the case of alcohol, inhibition develops with oxidation and retardation results until the oxidation of the inhibitor reaches a maximum. Thus, when chloroform is "preserved" with alcohol, the preservative is gradually consumed and is eventually totally destroyed, after which the decomposition of the chloroform itself proceeds as in the case of pure chloroform, with the exception that chlorinated derivatives of the oxidation products of alcohol may result.

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[17] The decomposition of commercial hypochlorite of soda is very largely due to the presence of small quantities of iron as ferrate in the liquor. Musspratt and Smith, *J. Soc. Chem. Ind.* (1898), xvii, 1096; (1899), xviii, 210.

[18] Baskerville and Hamor, *loc. cit.*

The Storage of Anæsthetic Chloroform.—Anæsthetic chloroform should preferably be furnished in vials or bottles of high grade anactinic glass,[19] containing about the quantity sufficient for one narcosis, and at the most not more than can be used within several days. If, for any particular reason, chloroform is ordered in a large container, it is advisable, immediately after opening it, to subdivide the entire remaining contents into two-ounce bottles, taking care to fill the small bottles completely. It is important to see that the bottles are completely free from water, and empty bottles should not be refilled without thoroughly cleansing and drying them. In no case should chloroform be gradually withdrawn in small quantities from large bottles or carboys. When it is found necessary to store anæsthetic chloroform, it should always be kept in a cool, dark place, in well-filled, or, better still, completely filled, tightly stoppered bottles of anactinic glass.

The condition of officinal chloroform which may be transported across the ocean and continent, or kept at sea for variable lengths of time, where it would be subjected to constant agitation, has been investigated. Anæsthetic chloroform in unopened, brown glass bottles were subjected to intermittent agitation for over 200 hours in a Spiegelberg shaking apparatus, and it was learned from four samples so treated that it is desirable to prevent the presence of air, *i.e.*, oxygen, being in association with this anæsthetic when it is to be shipped in the usual manner. Mouneyrat devised a method of displacing air by nitrogen, even making a nitrogen siphon of chloroform.

The keeping qualities of anæsthetic chloroform may be seriously affected by the character of containers. The question of keeping anæsthetic chloroform in tin containers has been a much agitated one in the Federal War Department, and within the last ten years this Department has decided in favor of the tin container.

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[19] The glass should show no alkaline reaction when the bottle is filled with distilled water containing several drops of phenolphthalein solution and heated at 100° C. for six hours. On the action of alkalies on chloroform, see Berthelot, *Bull. soc. chim.*, (2), xxix, 4; Andre, *Compt. rend.*, cii, 553; de St. Martin, *ibid.*, cvi, 492; and Mossler, *Monatsh.*, xxix, 573. It appears to be established that potassium hydroxide in alcoholic solution will slowly decompose chloroform.

The opinion of the author is that glass containers are more conducive to purity for several reasons: First, in cleaning the vessels any foreign matters present may be readily observed and the bottles properly cleaned. Second, in the case of tins, some of the flux used in soldering may be introduced and thus impart an acid reaction to the chloroform. Hydrochloric acid accelerates the decomposition of chloroform. The introduction of this flux is also a problem in ether manufacture which requires the utmost care.

Since it has been stated that spirit containing 95 to 96 per cent. by volume of ethyl alcohol is perfectly indifferent to tin, and tin and tinned metals are absolutely unattacked by 90 per cent. denatured spirit, the tinned metals only being corroded where the tin layer is broken,[20] one would conclude that acid-free chloroform,[21] containing the usual amounts of alcohol and water, would also be without action on tin, providing it is stored in tin containers, having no broken or scratched surface, very carefully capped, and with a minimum amount of air. In order to determine this, a five-pound sample of chloroform containing 0.84 per cent. by volume of absolute alcohol and approximately 0.05 per cent. of water, which had been stored in a tin container, sealed, for sixteen months, was examined for the presence of tin. This sample left a residue non-volatile at 100° C., amounting to 0.0220 Gm. per litre, but none remained upon ignition and no tin could be detected in the sample. The examination of a sample of anæsthetic chloroform which had been kept in a sealed tin for six years also showed that no tin had been dissolved. In both cases, however, oxidation of the alcohol present had occurred, although no decomposition products of chloroform were present.

Third, we have been informed by H. H. Dow [22] that he has "demonstrated that moist chloroform in the presence of a metal will slowly form traces of CH_2Cl_2 and . . . that it is pos-

[20] Heinzelmann, *Z. Spiritusind.*, xxvii, 339. Malmejac, however (*J. Pharm. Chim.*, 1901, xiii, 169) found that a small amount of tin goes into solution in 95° alcohol after six months.

[21] On the action of hydrochloric acid in chloroform on tin, see Patten, *J. Physical Chem.*, vii, 161, who found that the dry solutions act upon the metal less violently than upon zinc or aluminium, but more violently than on lead.

[22] Private communication.

sible to distil pure, dry chloroform in a metal container and produce a decomposition as shown by the following formula:

$$4CHCl_3 + 2Cu = C_2Cl_6 + 2CH_2Cl_2 + Cu_2Cl_2.$$

This reaction, however, takes place so slowly that it would never be noticed except in the handling of a material on which superlative efforts have been expended for years in order to get the last extreme of purity." Moreover, "all chloroform contains traces of CH_2Cl_2." In this connection, it should also be mentioned that it is probable that all metals which show anomalous anodic conductivity are likely to develop free hydrogen dioxide in contact with water and oxygen;[23] in the author's opinion, the presence of such metals should therefore be guarded against in the selection of a container for anæsthetic chloroform.[24]

The Pharmacopœia of the United States formerly required the use of "glass-stoppered" bottles, but subsequently changed this to "well-stoppered" bottles, thus allowing the use of cork stoppers, a practice which has become general in this country.[25]

The objections which have been urged against the employment of cork stoppers are two in number: First, the chloroform penetrates the cork after some time, especially during the agitation incidental to shipment, causing shrinkage and perhaps consequent leakage.

Allain [26] and Masson [27] have recommended that when chloroform is kept in cork-stoppered bottles, a lute of "bichromate gelatin" should be used to prevent leakage. This is unnecessary when a proper stopper is used and the employment of lutings on the stoppers has led to differences between the manufacturer and consumer in the past. Only one of the many samples of anæsthetic chloroform examined by the author was contained in a bottle having a luted cork stopper, and in this case, considerable

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[23] All of the manufacturers of chloroform in this country use brown glass ("anactinic") bottles. Of the eight different makes of German chloroform examined by the authors, only two were contained in colorless bottles.

[24] Barnes and Shearer, *J. Physical Chem.*, xii, 155, 468.

[25] In Germany, however, glass-stoppered bottles are used by prominent producers of anæsthetic chloroform (Kahlbaum; de Haen; Merck; A.-G. für Anilin-Fabrikation).

[26] *J. Pharm. Chim.*, (3), ix, 571.

[27] *Ibid.*, (6), ix, 568.

organic matter had been taken up, and, as a result, the chloroform failed to comply with the important sulphuric acid test or confused its interpretation.

The second objection is that organic matter is extracted from the cork and the chloroform fails when the sulphuric acid test is applied. To obviate these difficulties, certain manufacturers of chloroform have adopted the plan of covering the bottom of the corks with tin foil, a procedure which so far has been found to be satisfactory, but which may be open to some of the objections to tin containers. Other manufacturers use a paper or parchment covering, and still others select only the best corks and extract them thoroughly with chloroform before use.

The impurities of anæsthetic chloroform, so-called "organic impurities," are traceable to the materials used in the making, method of manufacturing, subsequent purification, manipulation before marketing, which may be grouped into one class (A), and those developed with different conditions of storage (Class B).

These impurities, even though some may not be of much importance from a physiological stand-point, must still be given attention, since an impure chloroform is more likely to become altered through oxidation during storage, notwithstanding the fact that pure ethyl alcohol has been added. So far as we have been able to learn, the adulteration of anæsthetic chloroform is not practised now, and crude chloroform is no longer sold as chloroform of anæsthetic grade.

In the first class (A) we have:

Excess water;
Excess alcohol;
Acetone;
Methyl alcohol;
Carbon tetrachloride;
Carbon dichloride (C_2Cl_4), carbon trichloride (C_2Cl_6), etc.;
Aldehydes;
Amyl, propyl, and butyl alcohols, and compounds;
Ether [25];
Acids (sulphuric, hydrochloric, acetic);
Metallic chlorides;
Ethyl chloride;

[25] From 1865–1875 ether was considered as one of the general contaminants of chloroform.

Ethylene chloride;
Ethylidene chloride[29];
Ethyl acetate;
Oils ("empyreumatic," "pyrogenous," "chlorinated");
Fixed and extractive matter.

The possible impurities under the head of Class B are as follows:

Acetaldehyde;
Acetic acid;
Carbonyl chloride;
Hydrochloric acid;
Hydrogen dioxide;
Chlorine;
Chlorinated derivatives of alcohol oxidation products.

You are spared a discussion of the numerous tests for these substances, as that discussion would of necessity involve much detail and be of interest mainly to the analytical chemist. Suffice it to say that in our laboratory we have studied every test we have been able to find in the literature and have been forced to devise new ones in some cases, while in others, we are unable to make any recommendations at all as yet. Two illustrations may prove of interest. Paraffin oil, sp. gr. 0.88, may be used to discriminate between 0.08 and 0.09 per cent. of water in chloroform, but it does not show the presence of a smaller amount. We are not aware of any test having been devised to show the presence of less than 0.05 per cent. of water in chloroform, until we found that crystals of calcium carbide would answer most satisfactorily.

Carbon tetrachloride boils at + 78.1° C. and has a specific gravity of 1.63; chloroform boils at + 61.2° C. and has a specific gravity of 1.4989. A binary mixture containing 7.8 per cent. carbon tetrachloride boils at + 62° C. From what has been said of the presence of the variables, alcohol and water, in anæsthetic chloroform and their influence upon the physical properties of chloroform, it will be quite evident that determinations of these physical constants can be of little real value, and their application in general practice, even in well-equipped laboratories, is

[29] About 1880 ethylidene chloride was regarded as a general impurity of chloroform.

quite out of the question. All our efforts to secure a method applicable on a laboratory scale to detect small amounts of carbon tetrachloride in chloroform have been unsuccessful. To be sure carbon tetrachloride possesses anæsthetic properties, but it must exert its own specific physiological effect and the anæsthetist should know the drug he uses.

Among the anæsthetic mixtures, the combination of chloroform vapor with oxygen was used shortly after the introduction of chloroform as an anæsthetic, and it has recently been reintroduced into practice. Hence it was important to investigate the changes which anæsthetic chloroform undergoes when a current of oxygen is conducted through it. Dr. J. T. Gwathmey [30] has recently stated that oxygen increases the value of all inhalation anæsthetics as regards life.

Several experiments were carried out in order to determine whether the passage of a current of oxygen through anæsthetic chloroform brings about decomposition of the anæsthetic. Anæsthetic chloroforms containing 0.56 to 1.0 per cent. of alcohol and 0.03 to 0.05 per cent. water were used. The conditions were such, except that the temperature was about + 20° C., as obtain during administration by the Gwathmey method, his apparatus being used. The oxygen was allowed to flow at such rates through 3½ to 4 ounces of the anæsthetic that about one-half remained in the vaporizer after 3½ to 10½ hours. In one experiment the chloroform vapor was passed through water as is Dr. Gwathmey's practice, and subsequently condensed. The examination of the residue and condensed chloroform showed the following:

Acidity (acetic acid):

Chloroform used	none.
Residue in container	0.00015 g. in 100 c.c.
Condensed chloroform	none.

Sulphuric acid test:

Chloroform used	negative.
Residue in container	marked reaction.
Condensed chloroform	negative.

[30] The writer has been collaborating with Dr. Gwathmey, who has directed the clinical observations.

Therefore it was concluded that the oxidation products of alcohol are not carried over when the chloroform-oxygen stream is conducted through water, and that these are concentrated in the residue. By this method of administration the patient is protected from the objectionable decomposition products even if they have developed. Furthermore, the vapors of the anæsthetic so applied are saturated with water, hence cannot exert that dessicating effect upon the mucous membrane they would if not moisture laden.

OXYGEN.

As animadverted, ninety-four years after the discovery of nitrous oxide and oxygen by Priestley, they were first used in combination for anæsthetic purposes. Although Andrews published accounts of several cases in which, by mixing oxygen with nitrous oxide, he had obtained a more satisfactory form of anæsthesia than with nitrous oxide alone, his observations failed to attract the attention they deserved. Ten years later (1878) Paul Bert drew further attention to this form of anæsthesia. Hewitt [31] stated, previous to the completion of the work reported this evening, that the most recent and best development in modern anæsthetics is the combination of oxygen with nitrous oxide, whereby a non-asphyxial and safe form of anæsthesia may be produced. The results of a long series of experiments with various anæsthetics and different mixtures caused Gwathmey to say "Oxygen is indicated with every anæsthetic and at all times. The longer the anæsthesia, the more urgent is the call for oxygen by the blood." The importance of the purity of the oxygen used is apparent.

The alchemists [32] were probably acquainted with oxygen, perhaps also the Greeks [33] in the fifth century, and the Chinese,[34] long before Priestley's experiments. In 1630, Jean Rey [35] knew that certain metals, when heated, fix a portion of the air, and in

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[31] "Anæsthetics," The Macmillan Co.

[32] Bolton, *Am. Chem.*, iv, 170.

[33] Hoefer, *Histoire de la Chimie*, ii, 271.

[34] Duckwood, *Chem. News*, liii, 250.

[35] Jean Rey, *Essai sur la recherche de la cause pour la quelle l'estain et le plomb augmentent de poids quand on les calcine*, Bazas, 1630.

1674 Mayow [36] prepared oxygen from nitre. In 1771, Scheele [37] prepared the gas by heating several oxides including the black oxide of manganese, and at about the same time Cavendish [38] studied oxygen. To Priestley,[39] however, has been given the honor of discovering oxygen as a constituent of the air. Davy [40] and Lavoisier [41] later studied the preparation and nature of this gas.

At the present time there are the following methods of preparation and manufacture of oxygen: [42]

1. Heating chlorates;
2. Heating chlorates with various substances;
3. From hypochlorites and reaction of chlorine and water;
4. Heating sulphuric acid or sulphates;
5. Heating various solids and mixtures (MnO_2, CuB_4O_7, etc.);
6. Combustion of solid mixtures (chlorates with combustible material, alkaline peroxides with hydrated salts, etc.);
7. Reaction of peroxides (ozone) with water and aqueous solutions;
8. By electrolysis of water;
9. From the air by means of mercury, cuprous chloride, barium dioxide; manganates, plumbates, or living matter; dialysis or absorption; and
10. From liquid air.

Oxygen that is to be used in anæsthesia should contain at least 95 per cent. O_2 upon the dry basis. We found the pyrogallate method for the determination of oxygen the most convenient to employ and most satisfactory provided Hempel's [43] precautions to prevent the production of carbon monoxide are taken.

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[36] Rodwell, *Chem. News*, viii, 114.

[37] *Abhandlung von der Luft und dem Feuer*, Upsala u. Leipzig, 1777.

[38] *Trans. Roy. Soc.*, lvi, 432; lxxiv, 119, 170; lxxv, 372.

[39] *Trans. Roy. Soc.*, lxii, 147; lxv, 384; lxxiii, 398; lxxv, 279; lxxviii, 147, 313; lxxix, 7, 289. "Experiments and Observations on Different Kind of Air," London, 1775–1777, ii, 29; iii, 1; "Experiments and Observations Relating to Various Branches of Natural Philosophy," London, 1779, i, 192.

[40] *Trans. Roy. Soc.*, ci, 1.

[41] *Chem. J.* (Crell), iv. 440; v, 125, *Crell. Chem. Ann.* (1786), i, 33, 136; (1788), i, 354, 441, 528, 550, 552; ii, 55, 262, 431, 433; (1789), i, 145, 162, 260, 323; ii, 68, 145, 433; (1790), i, 69, 518; (1791), i, 71; (1803), i, 29.

[42] Baskerville and Stevenson, *J. Ind. and Eng. Chem.*, iii, No. 7.

[43] Hempel, "Gas Analysis," English translation by Dennis, 1906, p. 149.

The following sorts of matter may be suspected to exist in a cylinder of compressed oxygen:

1. Solids.
2. Liquids.
3. Gases and vapors:

H_2O,
Halogen acids, HNO_3, organic acids,
O_3, NO_2, N_2O_3, SO_2,
NH_3, organic bases,
CO_2, halogens, oxides of chlorine,
HCN, $(CN)_2$,
PH_3, SbH_3, AsH_3, H_2S,
H_2,
CO, CH_4, organic matter,
N_2, N_2O, rare gases of atmosphere.

For these impurities, some of which are harmless from a physiological point of view, a qualitative search should be made

TABLE X.

No.	Source of oxygen.	O_2	H_2O	CO_2	H_2	Organic matter.	N_2, etc.	All other impurities.
1	$KClO_3 + MnO_2$	93.20	0.30	0.11	0	0	6.39	0
2	$KClO_3 + MnO_2$	98.31	0.14	present	0	0	1.54	0
3	$KClO_3 + MnO_2$	92.82	0.26	trace	0	0	6.92	0
4	$KClO_3 + MnO_2$	97.13	0.23	present	0	trace	2.63	0
5	Liquid air	96.10	0.15	0.01	0	0	3.74	0
6	Electrolysis	99.23	0.35	0.03	0.14	0	0.25	0
7	$Na_2O_2 + H_2O$	99.20	0.50	trace	0	0	0.30	0

and then, whenever necessary, a quantitative determination. A systematic procedure was devised which need not be gone into here.

Nitrogen and the "noble gases" may be determined by difference. It may be mentioned that no sensitive test is known for nitrous oxide.

Analyses, by our methods, of oxygen on the American market gave the results shown in Table X.

CONCLUSIONS.

I realize the danger of a mere chemist making an excursion into the field of medicine, but the extremely venturous one, if he has luck, may be swept by the rocks of which he is supposed to

have little knowledge. But I have done enough in this field to make me take a theoretical plunge.

Modern studies in physiology have unquestionably shown that the animal body exists to a great extent by virtue of the chemical and physical changes going on within it. I know of no valid reason for assuming that these changes are essentially different from those we control in the laboratory. If we wish to duplicate or control a physical or chemical change in the laboratory, we must become familiar with all the factors and conditions. I know of only one class of such changes over which we have not as yet secured control, and in that class belong those processes which we term radio-active. I am not sure but that we even have indications pointing toward our control of these. One of the essential factors in controlling a chemical process is the quality of the material with which we are working. I cannot therefore but regard all published statistics as to the mortality attributed directly to the anæsthetic used as more or less worthless and that a large number of new cases must be observed to secure knowledge of the real physiological effect of the drug when carried into the system by the pulmonary route.

Impure foods, sophisticated intentionally or otherwise, may bring on disease. Impure drugs, concocted or otherwise, fail to produce the full effect planned by the physician in curing disease. I feel that the great lack of uniformity among the pharmacopœias of the world need not obtain, especially where the analytical methods are involved. True, as Remington has maintained, "the Pharmacopœia is a book of standards for medicines, and not for analytical chemists," yet the methods of standardizing should be comprehensive, accurate, and reliable, as well as rapid and as simple as possible. It is unquestionably impossible for every pharmacist to determine the quality of all his chemicals and drugs, but the druggist may easily apply simple tests to determine the purity of many, especially when these tests are decisive and simple. While the dispenser must largely depend upon the reliability of the manufacturer, he should, like the physician, be familiar with the changes which chemicals undergo when improperly stored, in order that he may not allow impurities to develop and may guard against their formation. What a step modern civilization would take, if the leading nations

decided to put forth an international standard pharmacopœia, revised in full each decennium, with annual supplements!

Idiosyncrasy has served to account in large part for untoward after-effects of anæsthetics and certain disagreeable consequences, as nausea and interference with some of the normal organic functions, as glycosuria and albuminuria; these have often been regarded as natural results of anæsthesia and taken for granted. They may now be largely obviated, and in many cases entirely avoided, by the use of anæsthetics that are free from impurities, and by improved methods of administration. These statements are based upon clinical evidence.

The main objectionable constituent in ether is acetaldehyde. American official ethers call for three to four per cent. of ethyl alcohol in accordance with an old theory. Alcohol is practically never free from water, and in the presence of water and oxygen forms oxidation products. The speeds of the changes depend upon conditions. It has been shown that the administration of moist ether, free from aldehyde, at body temperature, is rarely followed by nausea (less than ten per cent.) and the usual strain upon the kidneys is not observed.

Chloroform was formerly made mainly from alcohol and contained many of the normal impurities of the alcohol used. These were not removed by the methods of purification practised, nor are they removable now, except by elaborate methods of purification. These impurities doubtless have had much to do with the feeling of uncertainty in administering chloroform. Pure chloroform undergoes decomposition when exposed under certain conditions, such, for example, as the manner in which anæsthetic chloroform is dispensed in some drug stores and hospitals. A suitable amount of alcohol prevents this decomposition, shunting the change in composition to itself; hence anæsthetic chloroform should contain ethyl alcohol. But the conditions of transportation and keeping of this chloroform should be such as to reduce the change of alcohol to aldehyde and acetic acid to the minimum.

Nitrous oxide, ether, and chloroform, each exerts its specific physiologic effect in producing anæsthesia without asphyxiation, provided the respiratory and cardiac functions are maintained approximately normal. This may be, and is being, accomplished by administering these gasified drugs with sufficient oxygen not

have little knowledge. But I have done enough in this field to make me take a theoretical plunge.

Modern studies in physiology have unquestionably shown that the animal body exists to a great extent by virtue of the chemical and physical changes going on within it. I know of no valid reason for assuming that these changes are essentially different from those we control in the laboratory. If we wish to duplicate or control a physical or chemical change in the laboratory, we must become familiar with all the factors and conditions. I know of only one class of such changes over which we have not as yet secured control, and in that class belong those processes which we term radio-active. I am not sure but that we even have indications pointing toward our control of these. One of the essential factors in controlling a chemical process is the quality of the material with which we are working. I cannot therefore but regard all published statistics as to the mortality attributed directly to the anæsthetic used as more or less worthless and that a large number of new cases must be observed to secure knowledge of the real physiological effect of the drug when carried into the system by the pulmonary route.

Impure foods, sophisticated intentionally or otherwise, may bring on disease. Impure drugs, concocted or otherwise, fail to produce the full effect planned by the physician in curing disease. I feel that the great lack of uniformity among the pharmacopœias of the world need not obtain, especially where the analytical methods are involved. True, as Remington has maintained, "the Pharmacopœia is a book of standards for medicines, and not for analytical chemists," yet the methods of standardizing should be comprehensive, accurate, and reliable, as well as rapid and as simple as possible. It is unquestionably impossible for every pharmacist to determine the quality of all his chemicals and drugs, but the druggist may easily apply simple tests to determine the purity of many, especially when these tests are decisive and simple. While the dispenser must largely depend upon the reliability of the manufacturer, he should, like the physician, be familiar with the changes which chemicals undergo when improperly stored, in order that he may not allow impurities to develop and may guard against their formation. What a step modern civilization would take, if the leading nations

decided to put forth an international standard pharmacopœia, revised in full each decennium, with annual supplements!

Idiosyncrasy has served to account in large part for untoward after-effects of anæsthetics and certain disagreeable consequences, as nausea and interference with some of the normal organic functions, as glycosuria and albuminuria; these have often been regarded as natural results of anæsthesia and taken for granted. They may now be largely obviated, and in many cases entirely avoided, by the use of anæsthetics that are free from impurities, and by improved methods of administration. These statements are based upon clinical evidence.

The main objectionable constituent in ether is acetaldehyde. American official ethers call for three to four per cent. of ethyl alcohol in accordance with an old theory. Alcohol is practically never free from water, and in the presence of water and oxygen forms oxidation products. The speeds of the changes depend upon conditions. It has been shown that the administration of moist ether, free from aldehyde, at body temperature, is rarely followed by nausea (less than ten per cent.) and the usual strain upon the kidneys is not observed.

Chloroform was formerly made mainly from alcohol and contained many of the normal impurities of the alcohol used. These were not removed by the methods of purification practised, nor are they removable now, except by elaborate methods of purification. These impurities doubtless have had much to do with the feeling of uncertainty in administering chloroform. Pure chloroform undergoes decomposition when exposed under certain conditions, such, for example, as the manner in which anæsthetic chloroform is dispensed in some drug stores and hospitals. A suitable amount of alcohol prevents this decomposition, shunting the change in composition to itself; hence anæsthetic chloroform should contain ethyl alcohol. But the conditions of transportation and keeping of this chloroform should be such as to reduce the change of alcohol to aldehyde and acetic acid to the minimum.

Nitrous oxide, ether, and chloroform, each exerts its specific physiologic effect in producing anæsthesia without asphyxiation, provided the respiratory and cardiac functions are maintained approximately normal. This may be, and is being, accomplished by administering these gasified drugs with sufficient oxygen not

to interfere seriously with the normal function of the hæmoglobin of carrying oxygen to the capillaries and by maintaining the usual concentration of carbon dioxide in, and providing its regular elimination from, the blood. Other factors involved are temperature and moisture. The anæsthetics are carried into the system at body temperature. This may be and is being accomplished by warming, and, in the case of ether and chloroform, by passing the vapor through heated water, which, at body temperature, not only removes the aldehyde, but saturates the gas with moisture (Gwathmey method). The osmotic action of the alveolar cells is thus affected only to the extent of the densities of the gases introduced into the lungs and not, as normally is the case, by temperature (always lower) and dessication as well. In other words, by the application of the principles of modern physical chemistry, the numerous variables are so reduced as to secure the real physiological effect of the particular anæsthetic drug after it enters the system. Nitrous oxide and oxygen may be used for prolonged anæsthesia and successfully for eighty per cent. of surgical cases; furthermore, ether and chloroform may be used with equal safety. The real, and no supposititious, idiosyncrasy of the patient may be met. The expert anæsthetist may now not only make it possible for the surgeon to perform even greater miracles, but with more comfort to himself in his work, and with greater happiness and less discomfort to the patient.

Study of the Firefly. H. E. IVES. (*Phys. Rev.* xxxi, 637.)—In conjunction with Coblentz the author has described an investigation of the visible radiation from one variety of firefly (*Photinus pyralis*). This investigation differs from previous ones in the application of photography with color-sensitive plates. There are grounds for believing that the firefly's visible radiation is its total radiation. Experiments in the infra-red and the ultra-violet regions of the spectrum are described. The region from 0.2μ to 1.5μ was explored. The only radiation was in a narrow band at 0.57μ as previously found. The abdominal skin of the insect is proved to be transparent as far as 3. The light is apparently under the control of the insect and has none of the properties of true phosphorescence, but is due to some bio-chemical process, which there is no reason to suppose cannot be artificially produced by man.

THE DISTRIBUTION OF ORGANIC CONSTITUENTS IN SOILS.*

BY

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THERE have been isolated in these laboratories from soil organic matter since this work was begun a large number of compounds which are so varied in their composition, properties, and origin, that they may be said to cover fairly well the principal classes of compounds encountered in other lines of biochemistry, and therefore the knowledge in regard to the chemical relationship, origin and processes of change accumulated in such other lines can be directly applied to the understanding of the biochemical changes in soils and the constitution of soil organic matter. Previous to these investigations the only organic soil compounds mentioned are the mythical humic acid, ulmic acid, geic acid, crenic acid, apocrenic acid, humin and ulmin, all of which are shown to be complex mixtures and therefore non-existent.

Of the compounds thus far isolated, some contain only carbon and hydrogen; some carbon, hydrogen and oxygen; some carbon, hydrogen, oxygen and nitrogen; and some carbon, hydrogen, oxygen, nitrogen and phosphorus. These compounds fall into the following classes: (1) Paraffin hydrocarbons, represented by *hentriacontane;* (2) hydroxy-fatty acids represented by *α-monohydroxystearic acid* and *dihydroxystearic acid;* (3) organic acids of unknown constitution, represented by *agroceric acid, paraffinic acid, lignoceric acid,* and a number of *resin acids;* (4) esters and alcohols, represented by *agrosterol, phytosterol,*

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glycerides of fatty acids, and *resin esters;* (5) carbohydrates, represented by *pentosans* and *pentose sugars;* (6) hexone bases, represented by *histidine* and *arginine;* (7) pyrimidine derivatives, represented by *cytosine;* (8) purine bases, represented by *xanthine* and *hypoxanthine;* (9) pyridine derivatives, represented by *picoline carboxylic acid.*

In addition to those here mentioned, a number of others are already isolated and will be reported upon in later publications from this laboratory. The methods by which the above compounds were obtained and the full description of their chemical properties have been given elsewhere.[1] It is obvious that definite chemical information of this kind sheds much light upon the nature of soil organic matter and the processes going on in soils.

While the work along the lines already laid down in the isolation and identification of definite soil constituents was progressing, it seemed desirable, if not imperative, that an idea be gained of the extent to which such constituents are distributed in the soils of the United States. Having found a compound in one or two soils and devised a method for its isolation and identification, the question naturally arises: Is this compound peculiar to the soil from which it has been isolated or is it a general soil constituent? Does it appear in one and the same soil under all conditions or is it the result of special treatments or crop practices, etc.? It is obviously of the greatest importance to know under what soil conditions and in what soils or class of soils any particular compound or group of compounds exists in order that a true and comprehensive view of soil organic matter in these soils can be obtained. Such information is necessary for a well-balanced opinion on the nature of soil organic matter in general, and a thorough recognition of the abnormal characteristics of certain soil organic matter, that is, an ability to distinguish between what is normal and what is abnormal. A survey of a large number of soils from widely different regions was therefore made and a method devised for such examination.

This method consisted in the co-ordination of the separate

[1] The Isolation of Harmful Organic Substances from Soils, by Oswald Schreiner and Edmund C. Shorey, *Bul. 53, Bureau of Soils,* U. S. Dept. Agric. (1909). The Chemical Nature of Soil Organic Matter, by Oswald Schreiner and Edmund C. Shorey, *Bul. 74, Bureau of Soils,* U. S. Dept. Agric. (1910).

methods used in isolating these compounds, so as to form a more or less rigid scheme of procedure for treating a relatively small amount of soil. The investigation methods naturally involved the use of very large amounts of soil, sometimes many hundred pounds, amounts too large for practical handling of so extensive a survey as was contemplated in this work. A further motive in formulating a rigid scheme of examination applied to a reasonably small sample of soil was to encourage such work among other investigators and students of soil with a view to extending this work over a larger area with a greatly increased force, to the end that a most comprehensive survey of the occurrence of such constituents in soil may be had and that exact knowledge of the nature of organic matter in soils might be increased and stimulated.

The method employed in separating the compounds from the soils was essentially the same as that schematically represented in an earlier article in this JOURNAL.[2]

The results obtained on a number of samples from different localities by the application of the scheme outlined for the separation and identification of definite organic constituents in the soils are briefly given in the following paragraphs, the soils being grouped by States in which the samples were collected.

Maine.—Two samples of Orono clay from the vicinity of Oldtown, Me. In both samples were found pentosans, xanthine, and histidine and in one of the samples there was found in addition hypoxanthine.

Massachusetts.—Five samples from various parts of Boston Common, Boston, Mass. All of the samples showed the presence of pentosans, cytosine, hypoxanthine, and dihydroxystearic acid.

New York.—A sample of Volusia silt loam from Ontario County, N. Y., showed the presence in the surface soil of pentosans, cytosine, and histidine, and in the sample of subsoil there was found in addition to these compounds, hypoxanthine and dihydroxystearic acid.

A sample of Clyde loam from Orleans County, N. Y., contained in the surface soil pentosans, pentose sugars, histidine,

[2] Schreiner and Shorey, JOURNAL OF THE FRANKLIN INSTITUTE, clxxi, 295 (1911). See especially Buls. 53, 74, and 80 of the Bureau of Soils for details.

cytosine, hypoxanthine and dihydroxystearic acid. The sample of subsoil showed in addition to the above compounds the presence of xanthine.

The examination of a sample of muck soil from Orleans County, N. Y., showed in upper as well as lower layers of the muck the presence of pentosans, pentose sugars and histidine.

Pennsylvania.—A sample of Chester silt loam from the vicinity of Philadelphia, Pa., showed the presence of agroceric acid, pentosans, cytosine, arginine, xanthine, hypoxanthine, and dihydroxystearic acid.

A sample of Frankstown stony loam from Bedford County, Pa., contained in the surface soil pentosans, pentose sugars, histidine, and dihydroxystearic acid. The sample of subsoil, however, did not show the presence of dihydroxystearic acid, but did show the presence of the other compounds found in the surface soil.

Maryland.—In a sample of Elkton silt loam from the vicinity of Easton, Md., was found paraffinic acid, α-monohydroxystearic acid, pentosans, xanthine, and dihydroxystearic acid.

West Virginia.—Samples of both surface and subsoil of Dekalb silt loam from the vicinity of Ravenwood, W. Va., showed the presence of pentosans, pentose sugars, and histidine.

Kentucky.—A sample of Clarksville silt loam from the vicinity of Broadhead, Ky., on examination showed the presence of pentosans, pentose sugars, histidine and dihydroxystearic acid in the surface soil. In the subsoil the same compounds were found with the exception of dihydroxystearic acid.

North Carolina.—Investigations conducted on a peat soil from the region bordering Lake Mattamuskeet, N. C., revealed the presence of hentriacontane, lignoceric acid, phytosterol, several resin acids and resin esters.

Mississippi.—Investigation of a sample of Houston clay from Noxuluo County, Miss., showed it to contain histidine and arginine.

Texas.—A sample of Amarilla silt loam from Sherman County, Tex., showed the presence of pentosans, pentose sugars, and histidine in both surface and subsoil.

North Dakota.—A sample of Marshall clay from Fargo, N. D., under investigation, showed the presence of agrosterol, agroceric acid, xanthine and hypoxanthine.

In discussing the foregoing results it is not intended to dwell upon the origin of these substances in the soils examined. Suffice it, therefore, to merely recall here the facts more fully discussed in the earlier papers cited that soil organic matter consists of the debris of all plant and animal residues and that the individual constituents of soil organic matter comprise: (1) The accumulated substances not readily subject to change, existing in the same form as in the original plant or animal material, and, (2) all the decomposition products which would arise through any agency whatever from proteins, fats, lecithins, carbohydrates, alkaloids, terpenes and all other constituents of previous vegetation or animal occupation.

The above list comprises twenty-six samples from eleven States. From twenty-three of these soils pentosan was isolated; the other three had not been subjected to this examination. Two of these soils, however, indicate large amounts of pentosan to be present by the furfurol test, these two being the Marshall clay and the North Carolina peaty soil, as already reported.[3] It would appear, therefore, that pentosans are a general constituent of soil organic matter.

Pentose sugars are found in eleven of the soils. The test for pentose sugars was not made in the earlier samples examined, but it was found in all samples in which a test was made. It would appear, therefore, that pentose sugars or pentose-containing complexes, not pentosans, the chemistry of which will be reported on in later publications, are common constituents of soils.

Histidine is a primary decomposition product of protein material. Its occurrence in seventeen soils of the twenty-four examined for it indicates that this hexone base is a fairly common constituent of soils and shows, therefore, that the protein cleavage in the soil is similar to that brought about by chemical or other action in laboratory investigations. That histidine persists in the soil during and after protein decomposition may be due to the fact that it is more resistant to change than other compounds of similar nature and origin.

Arginine is a common cleavage product of protein, but has so far been found only in two soils and is probably not a soil constituent which persists for any length of time.

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[3] Shorey and Lathrop, *Jour. Amer. Chem. Soc.*, xxxii, 1680 (1910).

Cytosine is derived from the breaking down of nucleo-proteids and nucleic acids existing in all plant cells. The fact that it was found in ten soils out of twenty-three examined indicates that it may also be a rather common soil constituent and shows conclusively that the change of such constant complex plant constituents as nucleic acid progresses in the soil in the same manner as it does outside of the soil through chemical agencies better understood.

Xanthine and hypoxanthine exist in plants as such and like cytosine also result from the cleavage of nucleic acids and nucleo-proteids. They further result from other purine bases, guanine and adenine. It is, therefore, not possible to state at this time the direct source of the xanthine compounds in soils. It is probable that their occurrence will be traced to all these sources. Out of the twenty-four soils examined for these purine compounds, five contained xanthine and nine contained hypoxanthine, thus showing that these purine bases will probably be frequently encountered in soil work of this character. Some of the soils contained xanthine only and some hypoxanthine only. Four of the soils contained both. Hypoxanthine is more resistant to bacterial action and this may explain its more frequent occurrence in the soils tested.

Although agroceric acid, lignoceric acid, paraffinic acid, α-monohydroxystearic acid, as well as agrosterol, phytosterol, and hentriacontane are reported as having been found only once or twice in the above list of soils, no general statement covering their frequency or lack of frequency of occurrence is warranted.

Eleven out of the twenty-six soil samples contained dihydroxystearic acid; five of these, however, were from a single locality. An interesting fact which may prove to be important is that in only one case was dihydroxystearic acid found without either hypoxanthine or xanthine or both being found at the same time. In seven of the samples it was accompanied by hypoxanthine only, in two samples by hypoxanthine and xanthine and in one sample by xanthine only.

Many other soil samples have been examined for dihydroxystearic acid in these laboratories. Over eighty soil samples comprising soils from eighteen States, extending from Maine to Oregon and southward to Texas, of widely different origin, topography, texture, climate, drainage, and cropping, varying

from soils of the highest productivity to soils incapable of producing profitable crops were thus examined with the result that dihydroxystearic acid was quite frequently encountered. The details of this investigation of soils for dihydroxystearic acid are reported elsewhere,[4] but for the sake of completeness, the general results should be here given.

One-third of all the soils examined showed the presence of dihydroxystearic acid. It was found in virgin soil as well as in soils under long cultivation; in soils continually cropped as well as in soils under permanent sod; in soils from the Atlantic coast; in soils from the Pacific coast; and in soils from the Gulf States. This compound is, therefore, a common soil constituent and is likely to be encountered in soils anywhere. Its formation or its accumulation is doubtless due to local conditions in any one section, but these local soil conditions are not confined to any region of the United States and probably not to any country or continent. The frequent occurrence of dihydroxystearic acid is of special interest and significance because of its known harmful properties to plants.[5]

When the soils examined are separated into good and poor soils, as based on field observations, their relationship with dihydroxystearic acid is rather striking. Among the good soils only two contained dihydroxystearic acid and they were of only moderate productivity. Among the poor soils the percentage of those containing this compound was fifty-one. Of the soils which had a record for infertility, the dihydroxystearic acid was found in each and every case.

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[4] *Bul. 80, Bureau of Soils,* U. S. Dept. Agric. 1911.

[5] Some Effects of a Harmful Organic Soil Constituent, by Oswald Schreiner and J. J. Skinner, *Bul. 70, Bureau of Soils,* U. S. Dept. Agric. (1910).

Soft-Toned Bells in China. Consul SAMUEL L. GRACEY in Daily Consular Report. (*Brass World,* vii, 203.)—The Chinese use large bells of their own make in many of their temples and monasteries. All through Japan and China the tone of these bells is very soft and smooth, due to the superior quality of the material used and to the absence of iron clappers. The bells are never swung, but are always suspended in a fixed frame, and are sounded by striking them on the outer edge with a wooden mallet. The result is a marvellous softness and mellowness of tone.

Liège Metal. Consul BARTLEY F. YOST, in Daily Consular Report. (*Brass World,* vii, 217.)—This "Liège Metal" is of special interest to aerial navigators both for "heavier than air" and "lighter than air" craft. It is said to be 40 per cent. lighter than aluminum and has a density of 1.762. It is grayish-white in color, reflecting rays analogous to those of poorly worked aluminum. Its composition is: Magnesium 99.3 per cent., sodium 0.21, zinc 0.44, iron 0.01, and aluminum 0.04 per cent.

Changes in the Velocity of Hydration of Cement. P. ROHLAND. (*Z. Chem. Ind. Kolloide,* viii, 251.)—Electrolytes change the velocity of hydration, and the effect is greater when they are added in the dissolved than in the solid state, and is approximately proportional to the concentration. Sodium carbonate, aluminum chloride, and potassium monosulphide accelerate the velocity while potassium bichromate, borax and sulphates (except aluminum sulphate and alum) retard it. The hardening process essentially consists in a coagulation of the hydrolytically separated hydroxides of silicon, aluminum and iron.

Harmful Influence of Sulphate from Commercial Salt on Firing of Stoneware. M. SCHMIDT. (*Sprechsaal.,* xliv, 264.)—The commercial salt used in salt glazing usually contains sulphates, which spoil the appearance of the finished ware, especially in an oxidizing atmosphere. The thin layer of salt-glaze becomes saturated with sulphates, which are either displaced by the silica of the body with evolution of gas and consequent bubbling of the surface, or else a separation of "galls" occurs. Sulphates are especially harmful, if salting begins before a full fire. The best way to avoid their action is to keep a reducing atmosphere in the kilns, till the last stage, when the fires are cleaned and air let through the grates. This reduces and eliminates the sulphates before the kiln reaches its highest temperature. But there is a risk of sacrificing the color of the body from the incomplete oxidation of the iron salts. The undecomposed sulphates are deposited on the walls of the kiln, take up water and percolate into the firebrick, where they separate out again and destroy the kiln. Sodium sulphate is more destructive than calcium sulphate.

NEW USES OF EXPLOSIVES IN AGRICULTURE.

BY

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BLASTING EXPLOSIVES have been used for a good many years for clearing new land of stumps and boulders and for cleaning up an occasional obstruction of this kind from land already under cultivation. Naturally the quantity of explosives required for this purpose has not been great because most of the larger farms started in the past twenty years are on prairie land where there are neither stumps nor boulders. An exception to this is found, however, in the Pacific Northwest where but little land is available for farms or orchards except that which is covered with stumps of great size. Here, land companies do the clearing on a large scale and use many carloads of dynamite every year.

The employment of explosives for clearing land cannot, however, be considered in any sense a new idea and farmers in all of those parts of this country where stumps or boulders have existed are well acquainted with its value for getting rid of them.

The new idea in farming to-day and one which bids fair to have remarkable and far-reaching results in relation to the growth and bearing of trees and plants is the deepening of the moisture-holding and vegetation-producing surface soil by using dynamite. The increasing demarkation between our wet and dry seasons, has made it necessary to adopt some artificial method of distributing more evenly to vegetation the moisture requisite to its proper development.

The first plan for overcoming uneven moisture distribution was a system of draining and irrigating. This seemed logical and effective because it disposed of the surplus water of the wet season and provided that which had been lacking in the dry season. There were, however, drawbacks to this plan, the principal ones being the prohibitive cost to private enterprise of systems of any considerable capacity, the impossibility of establishing them at any cost in certain localities and the forming of "alkali soil" by superirrigation in many places where draining and irrigating had been in effect for a few years.

Next, the soil-deepening theory was propounded. This was evidently a capital idea because it not only disposed of the surplus water of the wet season by making it possible for it to sink deep into the soil to be conserved there until it was drawn up when needed by the plants in the dry season, but it also provided open soil for plant roots to develop through, and made available to the plants a greatly increased quantity of the soil foods which they require. It appeared at first that deeper plowing would answer the purpose and it was strongly advocated by many agricultural authorities. The difficulty about deep plowing is that in many localities the subsoil is entirely unfitted for plant food until it has been exposed to sunlight, air and rain for a year or more. As the ordinary plow always turns the deepest soil that it reaches directly onto the surface, the depth of the surface soil could not be increased more than an inch or so each season without injuring the succeeding crops because the surface soil could not absorb a greater quantity of the subsoil and remain properly fertile. This was a very slow method of increasing the depth of the surface soil and was also limited because the ordinary plowing depth is only from five to eight inches with an occasional maximum of nine or ten inches, or twelve inches if the ground is plowed over the second time. The special subsoil plows go down fifteen to eighteen inches but they naturally require great power to operate.

With the drainage and irrigation idea almost prohibitive in cost and partly unsatisfactory in result, and the deep soil plowing plan slow and limited, the outlook for the establishment of new and maintenance of the old vegetation-producing areas in this country was not bright until the soil-blasting plan was suggested. It is not recorded just who first evolved this idea but it apparently originated in Kansas where in some places a very compact and well defined hard pan has prevented the satisfactory growing of crops. Samuel J. Crawford, once governor of Kansas, has been an advocate for some years of subsoil blasting, and it was his enthusiasm that led one of the large dynamite manufacturers to make an extensive study of the question a year ago which has resulted in demonstrations in the past six or eight months of its great value and practicability in many parts of the country.

The object when blasting subsoil is to shatter and break up a maximum area at a minimum cost without mixing it with the

surface soil. To do this it is necessary to vary slightly the kind of explosive, size of charge and spacing and depth of bore holes to comply with the different subsoil conditions met with in different places.

The usual custom, however, is to space the holes either fifteen feet or twenty feet apart, make them two and a half to five feet deep and explode in them a quarter pound or a half pound of slow-acting dynamite of 15 per cent. to 25 per cent. strength. If the holes are twenty feet apart and four or five feet deep, best results may be given by a half pound of 25 per cent. dynamite in each hole. If on the other hand, the holes are only two and a half feet deep and fifteen feet apart a quarter of a pound of 15 per cent. dynamite may be sufficient. With the four factors of spacing of bore holes, depth of bore holes, weight of charge and strength of explosive it is possible to adjust this work so as to exactly suit almost every soil condition encountered and a little experience with close observation will determine just how any particular piece of land can be most economically blasted. If there is any uncertainty about this and a considerable area is to be blasted, it is a good plan to try a few experimental shots at different depths and distances and with different quantities of explosives, then dig a hole with pick and shovel midway between the holes blasted and observe the effect of the blast on the subsoil. If there is any evidence of fissure or breaking midway between the holes, the blast can be considered satisfactory and the remainder of the work carried out accordingly. As the standard size dynamite cartridge for this work is 1¼ x 8 inches, which weighs approximately a half pound, the charges consist of either a half cartridge or a whole one.

It has been the custom to make the holes for subsoil blasting either with a dirt auger or with a pointed bar which is driven to the required depth with a sledge or maul. It is probable, however, that as subsoil blasting becomes more general, these primitive tools will be replaced by either geared hand drills or power drills. A power drill operated by a gasoline engine is now in use in some of the Western States. As the dynamite should expend as much force as possible in the subsoil, the holes must be filled compactly with damp clay tamping from the top of the dynamite charge to the surface of the ground. It is generally the custom to explode the charges with blasting cap and fuse.

When this is done the fuses are cut so that from four to six inches will extend above the ground after the charge has been properly tamped in the hole. These are then lighted one after the other. A small torch is very effective for the purpose but unless a high wind is blowing, matches may be used. If the charges are properly gauged, located and tamped, there should be only a slight disturbance of the surface of the ground when they explode.

Sometimes the charges are exploded electrically with a blasting machine. Then electric fuses are used instead of fuse and blasting cap and from ten to a hundred and fifty charges are exploded simultaneously, depending on the capacity of the blasting machine. This method may be a little more effective but is also a little more expensive.

When a clearly defined clay hard pan from two to five feet thick is to be blasted, best results will usually be had if the charge of explosives is located about six inches above the bottom of the hard pan.

The cost of blasting subsoil, including explosives, blasting supplies and labor is between twelve dollars and twenty dollars an acre and this is not infrequently paid for by the increase in the first crop after the blasting has been done. As the beneficial effect of the blasting lasts many years it can be readily seen that it is an excellent investment.

The quantity of explosives required to blast an acre of ground with bore holes spaced at different intervals and loaded with different size charges is given in Table I.

TABLE I.

Distance between holes, feet.	No. of 1¼ x 8-inch cartridges in charge.	Approximate No. of pounds of dynamite per acre.
15	½	50
15	1	100
20	½	27½
20	1	55

Subsoil blasting is not only done on land producing cotton, cereals, small fruit, vegetables, etc., but has proven of great value in orchards. Here it helps to dig the hole for the new tree, makes ample room for roots to spread and provides a reservoir for conserving the moisture required to support the tree. After these orchards have begun bearing, and particularly in old

orchards where the trees are beginning to fail, root cramping, "wet feet," wet rot and many other obstructions to their growth, are overcome by blasting between the trees or in some cases directly under them. Blasting between the trees is done in the same way as other subsoil blasting except that the holes should not be less than four feet deep and the method of spacing them is governed by the distance apart the trees stand. A charge of a quarter of a pound of 25 per cent. dynamite in each hole, is generally sufficient.

When the trees are planted on the "square system" and are fifteen to twenty feet apart, the holes should be located midway between the trees on diagonal lines, making one hole to each tree (Chart I). Trees planted on the "square system" twenty-five or thirty feet apart require the holes for blasting midway between them on the square lines or an average of two holes to the tree (Chart II). If the trees are more than twenty-five feet apart three holes should be put down on three sides of the tree, about ten to fifteen feet away from it, these holes being located at the points of an equilateral triangle with the tree in the centre (Chart III).

Explosives are now being employed very largely for digging ditches. In much of this ditching dynamite does the whole thing and neither pick, shovel nor ditching machine is used. Although ditching may be done almost entirely with dynamite under nearly any condition, it is particularly economical and effective in swampy clay ground and many ditches are now dug with dynamite in land of this character. To dig these ditches holes are punched with sharp bars at intervals of two feet along the line of the proposed ditch, to a depth six or eight inches less than the ditch is to be. These holes are not perpendicular, but at an angle of from 25° to 45° with the perpendicular, and all pointed toward that side of the ditch where the material excavated is to be thrown. All of the holes but the middle one are loaded with one cartridge (1¼ x 8 inches) of 50 per cent. or 60 per cent. nitroglycerin dynamite. The middle hole is loaded last with two or three cartridges of the same explosive, one of which has been primed with a section of waterproof fuse and a No. 6 blasting cap. It is not ncessary to use tamping in any of the holes provided the ground is sufficiently swampy for water to cover the charge of explosives when it is in place in the bottom of the hole. The detonation of the charge in the middle

CHART I.

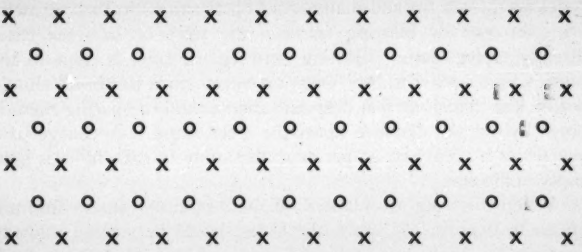

Diagram showing location of holes for blasting when trees are 15 feet to 20 feet apart.
X = tree; O = hole for dynamite.

CHART II.

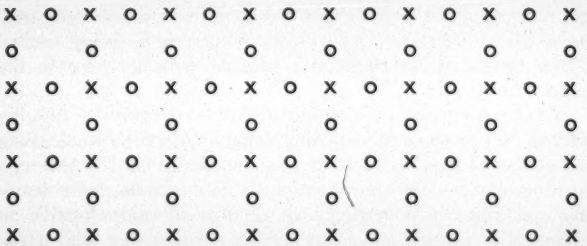

Diagram showing location of holes for blasting when trees are 25 feet to 30 feet apart.
X = tree; O = hole for dynamite.

CHART III.

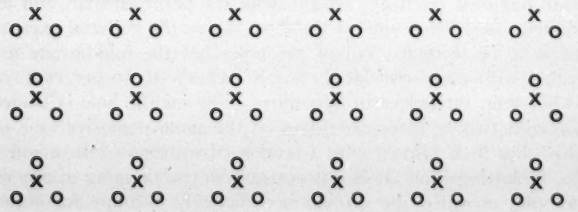

Diagram showing location of holes for blasting when trees are more than 30 feet apart.
X = tree; O = hole for dynamite.

hole communicates to the adjacent charge in both directions and so on, almost instantaneously to either end of the row and a comparatively regular ditch about three feet wide at the bottom, five feet wide at the top and from three feet to five feet deep, according to the depth of the holes, is the result. The length of the ditch which can be blasted at one time is only limited by the time required to charge the holes. A mile or more may be blasted simultaneously provided enough men are punching and loading the holes to finish the work quickly, but nothing is gained by attempting to blast so much at once that the dynamite in holes first loaded will be kept under the water longer than an hour or so before blasting. The middle hole is always charged just before blasting so that the blasting cap and fuse will not remain under water longer than a few minutes. This work should be done in comparatively warm weather because when most nitroglycerin dynamite has been under water having a temperature lower than 50° F. it is likely to become more or less insensitive, which might prevent the charges from exploding the adjoining ones. The explosion may also fail to communicate from one charge to another through dry soil and when ditches are dug in this ground, each charge should be primed. The additional expense brought about by priming each charge can, however, be offset to some extent by placing the charges farther apart, and using a lower grade and cheaper dynamite—30 per cent. to 40 per cent. usually being satisfactory. In damp clay soil it is not often necessary to prime each charge but they should not be spaced farther apart than eighteen inches. Ditches from six to ten feet wide are blasted with two parallel rows of holes, the rows being from eighteen inches to three feet apart. With three parallel rows of holes ditches fifteen feet wide at the top and five feet deep can be dug with dynamite.

Blasting ditches has several advantages over other methods. Under many conditions it is cheaper, usually costing eight to ten cents per cubic yard of excavation, including explosives and labor and with the material excavated all disposed of. It is always much quicker than any other method, three men, under ordinary conditions being able to dig a thousand feet or more in a day. In swampy land covered with stumps, trees and underbrush it is the only feasible method, and is little if any more expensive there than in open country as the blast clears out all

obstructions along the line of the ditch. It does not, like the hand or machine method of excavating, heap up the earth along the side of the ditch where it prevents drainage into the ditch and occupies ground that might be producing crops, but spreads it evenly over the adjoining land for some distance. Blasting also opens and fissures the ground on either side forming an almost perfect subsoil drainage into the ditch.

Blasted ditches are usually somewhat ragged looking at first but will square up almost immediately when the water enters them. They cave but little, if any, as the blast gives the sides a good slope.

When the location of ponds and swamps is such that the cost of draining them by ditching would be prohibitive, they can frequently be permanently dried up by blasting openings through the impervious subsoil underneath them which is responsible for their existence.

As this subsoil may be from five to thirty or more feet thick and the charge of dynamite should be located deep enough for it to break through into the stratum of sand, gravel or rock underneath, it is sometimes necessary to provide augers that will drill thirty feet deep. These augers are usually made by welding a two-inch dirt auger to a four-foot section of one inch or larger gas pipe. Other four-foot sections of the gas pipe, each with a collar or coupling, are also provided. The auger section is turned by means of a bar through a tee screwed on the upper end. As soon as this section is down as far as it will go, the tee is unscrewed, another section of pipe with the coupling permanently attached to the lower end is screwed on to the first section, and the tee is screwed to the second section. This process is repeated until the hole has reached the required depth. The explosive will usually give best results if located a foot or so above the bottom of the clay stratum, for if the charge is placed almost or quite in the more open stratum below it will expend its force in chambering that instead of shattering the clay above. It is necessary, of course, to use the first hole as a test hole and drill it down to the lower stratum. When the clay is underlaid by rock the charge of explosives should be put down on the rock. The explosion then breaks up the clay, opens fissures between the rock and the clay and may even crack and split the rock.

As this work is always wet, gelatin dynamite should be used. The 40 per cent. grade is about the proper

strength. Holes six to ten feet deep usually require about five cartridges, holes ten to twenty feet deep ten cartridges and holes twenty to thirty feet deep, fifteen cartridges of the 1¼ x 8 inch size. It will usually answer the purpose if the holes are forty to fifty feet apart. Sometimes two or three properly blasted holes put down in the lowest part will drain a large pond. The blasting should always be done electrically as a fuse is likely to give trouble under water. No tamping is required, the water in the holes answering the purpose.

If the surface water is more than a foot or so deep, the holes can be drilled and charged from a raft. After the auger has been withdrawn the cartridges of explosives can be pushed to the bottom of the hole, one or two at a time, with a long straight stick. If given a good firm push when they are at the bottom, they will remain in the proper position. It is well when loading to use a section of one and a half inch pipe pushed down a few inches into the hole and extending a foot above the surface of the water. The cartridge primed with the electric fuse should be loaded last or next to the last. Then the section of pipe used in loading the hole should be lifted over the upper end of the electric fuse wires. These wires must next be connected to the two leading wires which should be carefully paid out while the raft is poled a hundred feet or more from the hole. The free ends of the leading wires may then be attached to the blasting machine, the operation of which will explode the charge.

The use of dynamite for other work about the farm, such as grading roads; digging cellars; excavating trenches for foundations, pipe lines, tiling, etc.; digging holes for poles and fence posts and sinking wells is too well understood to require more than casual mention. Nevertheless all of this work is necessary and cannot be economically accomplished without using dynamite and using it according to approved methods.

The Red Cross explosives are generally preferred for most of the blasting necessary about the farm because they do not freeze so readily as many of the other high explosives and are also somewhat safer to handle. They are too insensitive, however, to use satisfactorily for ditching when the whole line of charges is to be detonated by the one in the middle, and the fumes which they give off when detonated are more objectionable in close work like well sinking than the fumes from gelatin dynamite.

Carbon Tetrachloride as a Fire Extinguisher. J. A. ROBINSON. (*Eng. News*, lxv, 326.)—The electrolytic preparation of chlorine has made carbon tetrachloride an inexpensive article. Carbon bisulphide treated with chlorine yields carbon tetrachloride and sulphur dichloride; the latter is decomposed by injecting sodium hydrate and the carbon tetrachloride is purified by distillation. Carbon tetrachloride is a colorless liquid which boils at 78°C., but is non-inflammable and non-explosive, and its vapors stifle fire. The Interborough Rapid Transit Co., of New York, use it in fire extinguishers, and it is said to be preferable to water and sand for extinguishing arcs in electric installations. According to E. A. Barrier, the addition of tetrachloride to naphtha renders it fire-safe, but it must be applied in considerable proportions; a 70°C. naphtha or motor gasoline should contain 60 per cent. of the tetrachloride to be safe against explosion, and 70 per cent. to be fire-safe.

New Method for Electroplating Aluminum. (*Brass World*, vii, 202.)—Carl Rümpler, of Schöneburg, near Berlin, has patented a new method of electroplating aluminum. He claims that if a slight film of a brass deposit (containing as much zinc as possible) is first put on, the other deposits may be put on in the usual manner. He recommends a brass which contains not less than 50 per cent. of copper. A small quantity of a haloid, *e.g.*, potassium chloride, bromide or iodide is used in the plating bath. The brass solution recommended contains potassium and copper cyanide 5 oz., potassium and zinc cyanide 2 oz., sodium sulphite 5 oz., potassium hydroxide 2 oz., potassium chloride 1 oz., water 1 gal. Use brass anodes, and a current of 1.8 volts with a density of 2 to 3.6 ampères per square decimeter. The time for the formation of the brass film is from 1 to 2 minutes. Then proceed as usual.

Gyroscopes as a Means to Stability in Aeroplanes. GIRARD VILLE. (*Comptes rend.*, clii, 127.)—The gyroscopes used weighed about 5 k.g. and rotated at 6000 revolutions per minute. The gyrostatic action was used to cause rudders to work automatically. Experiments with a fixed apparatus were tried in a uniform air current, and also in the variable winds at the top of the Eiffel tower. It was found that the gyroscope with its pivoted frame tended to acquire an oscillatory movement, which was overcome by the use of damping planes immersed in water. This difficulty was not experienced when the apparatus was applied to gliders 12 metres square in area, the planes themselves being sufficient to damp the oscillations. The gyroscopic governor successfully compensated for disturbances of balance due to distribution of load and to variable winds and was used to advantage in a motor-driven aeroplane.

THE TEACHING OF ELEMENTARY CHEMISTRY.*

BY

ROBERT H. BRADBURY, Ph.D.,

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I. COMPLEXITY OF THE PROBLEM.

CHEMICAL science is only about a century and a quarter old. As a special branch of knowledge, with its own objects and methods, it began with Lavoisier, who also wrote the first systematic text-book on the subject. The use of the laboratory as an aid in instruction dates only from the establishment of Liebig's laboratory at Giessen, in 1824. The High School laboratory is a recent phenomenon. It began only about thirty years ago and, even at present, laboratories are far from universal, while in many schools, the large size of the classes, the shortness of the laboratory period, the lack of all efficient laboratory assistance and the necessity of working up to a formal written examination throw grave difficulties in the way of the proper development of the work.

The High School treatment of chemistry is still in its formative stage, and this is especially true of the laboratory treatment, which is the more recent. The course in the classroom is prevented from taking any final definite shape by the rapid growth of the science. This growth perpetually produces new subject-matter which tends to displace the old. Electrochemical conceptions, which were hardly represented in the text-books a decade ago, now dominate the whole treatment of large sections of the course. Colloid chemistry and radio-chemistry have hardly penetrated into the texts as yet, but they are handled in some way or other by all High School teachers of chemistry. The practical applications of the science demand an increasing amount of attention.

So far as the experimental work is concerned, the whole matter of High School laboratory instruction is so new that no sort of general agreement has been reached with regard to

*Presented at the meeting of the Section of Physics and Chemistry held Thursday, May 4, 1911.

the most advantageous way of handling it. Whether the work should be all quantitative or all qualitative, or partly the one and partly the other are disputed questions. The fact that a qualitative exercise is hardly worth the time it takes, unless it is related in some very definite way to the general points of view of the science, seems to be scarcely appreciated as yet by the authors of text-books. The constant influx of new matter, both into the laboratory and class-room tends almost irresistibly to force the teacher into a kind of episodic treatment. He is obliged constantly to combat the tendency to allow his course to degenerate into a series of interesting but unrelated discussions of special topics, while the logical connecting structure which has produced all these developments, just as a tree produces its fruit, is slighted.

The time devoted to chemical science in the High School averages about four hours a week for a school year of forty weeks. Half of this time is spent in the laboratory. It is plain that this scanty allowance bears no relation to the educational value of the science, nor to its practical importance to the student. The time might be doubled with advantage by extending the course through two years, but it is difficult to see where the additional hours are to come from and our present problem is to do the best we can with the time we have.

II. THE TEXT-BOOK.

One of the invariable features of the text-books of our science has been, for many years, the preference exhibited for the non-metals as the subject-matter of the early part of the work. This is most noticeable in Hoffmann's classical "Moderne Chemie," [1] practically the whole of which is devoted to the non-metals and to the theory, the metals being scarcely referred to. In Friedrich Wöhler's excellent "Grundriss der unorganischen Chemie," [2] the first fifty pages are devoted to general theoretical matters, and in the succeeding hundred pages the non-metals and their compounds are discussed. The balance of the book (two hundred pages) is devoted to the metals, which are dealt with in a compact, precise and altogether masterly way. The difference

[1] 6te auflage (1877).
[2] 15te auflage (1873).

in the importance attached to the metals by these two great chemists is most interesting.

The modern text-book authors have followed Wöhler rather than Hoffmann. That is, they take up the non-metals first and use them as the raw material from which to evolve most of the important general principles of the science while the metals are handled mainly in the second half of the book. There are, however, some important departures from Wöhler's order, most of which appear to be the result, first of a desire to acquaint the student with at least one metal in the early portion of the work and second, of an attempt to arrange the order of topics with reference to materials more or less familiar to the student. This second principle of arrangement is a most important one, since it is really the basis of all first-rate scientific exposition and the current type of text does not, in my opinion, allow sufficient weight to it.

III. THE ORDER OF TOPICS.

Anyone who will attentively examine the chief texts in the field will be surprised at the sameness of the order of topics. It may be said that, broadly speaking, water, air, salt and the periodic law furnish the skeleton of the conventional book.

The book begins with a general chapter, dealing with the scope of the science, with physical and chemical change, with mixture, compound, element, solution, combination, decomposition, and so on. It is plain that the student cannot possibly understand these generalizations until he has had at least one specific instance of each.

The authors meet this difficulty by intercalating illustrative experiments and these are nearly the same in all the books—salt water for solution, iron and sulphur for combination, mercuric oxide for decomposition, etc. An alternative method and, one might well think, a better one, would be to begin directly with the descriptive chemistry and to handle the abstract general matters as specific examples occur naturally in the course of the work. Why begin to generalize before the student is familiar with the facts which at once necessitate the generalization, render it intelligible, and supply the material for it?

The descriptive matter now begins with chapters devoted to oxygen, hydrogen and water. Practically all the books

introduce the stochiometric laws, symbols, equations and the atomic and molecular theory at this stage. The use of water for the introduction of these generalizations began, I believe, with Hoffmann.

IV. AVOGADRO'S HYPOTHESIS.

Salt then serves to introduce chlorine and the atmosphere to introduce nitrogen and its compounds, after which the beginner, equipped with some knowledge of hydrochloric acid, ammonia, nitrous oxide, nitric oxide, etc., is considered ready to attack his *bête noire* Avogadro's hypothesis. In fact the course is arranged, up to this point, with the object of reaching Avogadro's hypothesis as rapidly as possible, so as to permit the use of molecular formulas (Compare Alexander Smith, "The Teaching of Chemistry," p. 54).

The universal trouble which beginners have with Avogadro's hypothesis is a curious phenomenon. In itself, the subject is not as difficult as some propositions in geometry, which the same students handle with ease. The difficulty is often due to the introduction of the subject before a sufficient foundation has been laid for it. Among the conceptions preliminary to Avogadro's hypothesis are those of gas, homogeneous substance, element, compound, mixture, atomic and molecular weight. These things are novel and difficult. They need to be treated in a practical and inductive rather than in a theoretical and dogmatic way. The last six ideas can hardly be imparted successfully without much laboratory work with *solids*, especially sulphur and the familiar metals.

When these seven conceptions have been deliberately worked out Avogadro's rule may be given, simply in *grams* and *litres* and enforced by illustrative problems. The molecular hypothetical presentation forms the natural conclusion of the subject. I have satisfied myself that the difficulties which beset the subject of Avogadro's hypothesis disappear if this course is followed. The only disadvantage is that the introduction of *molecular* formulæ is somewhat postponed, but this is not as serious as it looks at first sight. At present, we have decisive evidence for the molecular weights of gases and dissolved substances only. The innumerable formulæ of liquids and solids which we constantly employ are not truly molecular. HgO, FeS, NaCl, Na_2SO_4 and H_2O (liquid) are a few out of hundreds

of instances with which our text-books bristle. We are practically without evidence with respect to the molecular weights of these substances and the formulæ are merely the simplest expression of the percentage composition. Of course this does not interfere in the least with their use in equation-writing or in solving problems.

For this reason, it seems to me that the importance of the early introduction of molecular formulæ has been greatly exaggerated. For instance, there is little consistency, in the present state of our knowledge, in forcing the student to write

$$2HgO \rightarrow 2Hg + O_2$$

instead of

$$HgO \rightarrow Hg + O.$$

The first equation is no more a correct representation of the mechanism of the change than the second. When the conception of molecular weight becomes applicable to solids we may be obliged to use a still more complex equation, *e.g.*,

$$Hg_{10}O_{10} \rightarrow 10Hg + 5O_2$$

but, at present, the simplest equation is the easiest for the beginner to handle and also the most scientific, since it keeps within the limits of our knowledge of the matter. Obviously the same remarks apply to similar cases like

$$KClO_3 \rightarrow KCl + 3O.$$

V. RESIDUAL TOPICS.

The next subject is Van't Hoff's extension of Avogadro's hypothesis to solution, which lead up to ionization and to the completion of the topic of acids, bases and salts.

At this point—roughly speaking, the middle of the book—a certain divergence of opinion becomes apparent. According to the manner in which the latter half of the work is arranged, the texts can be divided into three classes:

1. Those in which there is a chapter on the periodic law somewhere near the middle of the book, the periodic classification being followed after this point.

2. Those in which the periodic classification is followed through the latter half of the book, but the formal discussion of the law itself is postponed to the end.

3. Those which make no attempt to follow the periodic classification, but discuss the law itself at the end, in the light of all the knowledge which the student has gathered.

Excellent texts have been written according to all three of these plans, but the teacher who tries all three methods will conclude that the third offers the fewest disadvantages. The first is of course the most systematic, but it is almost unworkable with average classes. In a subject to which only about two hours a week in the class-room can be given, it is impossible, in half a year, to bring students to a stage at which they are ready to grasp the periodic generalization. If the teacher can reach this point with his classes at the end of the year he has done well and has every reason to be gratified with the result of his labors.

As for the second plan, the method of giving the facts first, and then erecting the generalization upon them, is usually by far the best approach to any abstract topic. But the periodic law is an exception. The material summed up in it is too extensive for the student to retain it until the time arrives for the setting up of the generalization. To classify tin with carbon, gold with sodium, manganese with chlorine and to lay stress on non-existent oxides, in the hope that, when the time comes to study the periodic law, the student will reap some advantage, is little better than a waste of time. It is far better to classify the elements in the simplest and most natural way, and to add whatever modifications are necessary, from the periodic view-point, in the chapter devoted to that subject. If the law is then given a candid treatment, which calls attention not only to its dramatic achievements, but also to its numerous puzzling defects, the subject will arouse the keenest interest of the students and will serve at the same time, as a valuable review of a large portion of the material of the course.

VI. SUMMARY.

It may be well to point out that we are making the assumption that the arrangement of the work is the same as that of the text employed, so that it is unnecessary to discuss the two separately. Thus far, we have devoted ourselves to what may be called, in no disparaging sense, the *conventional* type of book. At this stage it will be useful to sum up the results of our examination.

(*a*) The conventional text is constructed with the object of teaching the student the facts and results of chemical science, so far as possible during the very limited time available. The knowledge which it seeks to give is of the kind which can readily be tested by a written examination.

(*b*) As an essential feature of this programme, the stress is laid wholly upon the *subject-matter* while the *method* of the science is hardly noticed at all. Thus, a student who has mastered the treatment of the atmosphere in the current type of text will have a rather complete knowledge of the properties of the different gaseous constituents and the proportions in which they are present. With respect to the way in which all this knowledge has been acquired, or to the way in which he might go to work to investigate the matter for himself, he will have only the haziest ideas. If his knowledge is called into question, he will probably be unable to defend it, except by reference to the books where the statements are to be found. The conventional text is almost wholly dogmatic—as distinguished from inductive—in its presentation. Everything is communicated—hardly anything is proved. Little space is given to the historical side of the science, for teaching chemistry along historical lines is almost the same thing as teaching it inductively. In both plans, the effort is to show how the generalizations arise out of the facts and both will, in at least nine cases out of ten, lead to the same order of presentation of a topic.

(*c*) Another aspect of dogmatic presentation is that the orderly development of the student's ideas, which is really the whole object of the work, is relegated to the background as a minor matter, the main aim being to achieve a compact, accurate, systematic statement of the facts and principles the student is to learn. In this the shadow cast by the impending examination is plain.

The desire for compactness is probably responsible for the way in which substances and processes totally strange to the student are employed at the beginning of the work. In the introductory chapter of his text the student usually finds himself confronted with sulphuric, nitric, and hydrochloric acids with mercuric oxide, potassium chlorate, silver nitrate, sodium and carbon disulphide, with solution, crystallization and electrolysis.

I venture to think that there has been too much of this

sort of thing. It is, of course, an important part of our business to enlarge the student's knowledge of the elements and their compounds, but the enlarging should be done in a logical way. The introduction of an unfamiliar substance, before the time has come for its full discussion, is a serious evil, and it is an evil which can usually be avoided by a little care in the arrangement of the work.

VII. THE HEURISTIC METHOD.

We may permit ourselves, then, to indulge in the paradox that the current type of chemical text is essentially a *popularized* form of chemical science. It is popular in the sense that its leading aim is to achieve a general survey of the results of the science, without much reference to the process by which those results are obtained. Strictly scientific literature contains not only certain results of investigation, but also the rigorous evidence which will convince all normal men, who will take the trouble to analyze it, that those results are correct.

The *heuristic* method which, under the energetic advocacy of Prof. Armstrong, has had a profound effect upon the teaching of our science in England—abandons, at the start, all idea of making a systematic survey of the subject. The stress is laid, not upon the results, but upon the method of the science, and the student is put in the attitude of an investigator from the first. The early part of the work is confined to familiar materials, such as sulphur and the common metals, water, air, salt and pyrite. The facts obtained by simple experiments are gradually organized, without any effort to hurry the development of the generalizations.

There is no doubt that the advocates of the heuristic method have grasped an educational factor of great importance. The objection often made that it is useless to train students in research because so few of them will become investigators is no answer to their contention. Research is simply the solving of problems by observation and experiment and every man whose function requires something more than mere routine work is of necessity continually engaged in investigation. The problem, for instance, of reducing the cost of a manufacturing process is fundamentally scientific and is to be solved by methods very similar to those which enable a student to ascertain whether copper and sulphur do or do not unite in fixed proportions by

weight. And there can be no question that the ability to attack a problem aggressively by experiment and to think accurately in interpreting the results is far more valuable, as a preparation for life, than even the most encyclopedic knowledge of facts.

Much damage has been done the heuristic method by the extravagant claims of some of its friends. Consider, for instance, this passage from Arendt[3]: "Die Schüler haben die den chemischen Erscheinungen zugrunde liegenden Ursachen selbst auszufinden und die zum Ziele führenden Versuche und die Art ihrer Ausführung anszudenken. Der Versuch werde stets zur Erforshung einer Ursache veranstaltet; die Theorie werde aus der Beobachtung entwickelt, und zwar müssen die Schüler die allgemeinen Begriffe und Regeln selbst ableiten."

The services which Prof. Arendt has rendered to chemical education are great, but this particular passage is little better than pure nonsense. A course in which the student was required to recreate the science—experiments, theory and general principles—for himself would be wholly unworkable, for it assumes the possession of superhuman intelligence. The great investigators have won their imperishable renown by doing, for small portions of the science, exactly what Arendt would require each student to do for the whole subject. Supposing that the start was made in the simplest possible manner by heating sulphur with familiar metals, it is doubtful whether the student would come unassisted to the conclusion that the substances supplied to him were elements and that he was dealing with cases of combination.

VIII. COMPROMISE.

It will not answer simply to assume that the student must find out everything for himself, for this would forbid all progress. How much he is to find out and how much is to be communicated to him must be decided by careful consideration of each topic. For instance, the proof that copper and sulphur are elements is clearly beyond the powers, not only of the beginner, but also of the advanced student. But *assuming* that copper and sulphur are elements, the proof that, when heated together, they combine in definite proportions by weight forms an exercise which the beginner will work out with surprising enthusiasm and exactness.

[3] Compare *Zeitschr. für Phys. u. Chem. Unterricht*, vol. xxii, p. 192.

The intelligent, practical limitation of the heuristic method forms a complex problem which has been most successfully solved, so far as I know, by Otto Ohmann of the Dorotheenstädtischen Realgymnasium at Berlin.

In handling the atmosphere, for instance, the usual course is to describe oxygen, to describe nitrogen, to tell the student that these two gases in certain proportions make up the chief part of the air, which, however, contains smaller quantities of other substances, and so on.

Before attacking the atmosphere, Ohmann's book[4] gives the student an opportunity—from work with sulphur, the familiar metals and some mineral sulphides—to form the conception of element, compound and mixture. The chemical study of the air is then begun by investigating the effect of heating metals in it, at first qualitatively and then with reference to increase in weight. By heating a folded piece of sheet copper and noting the absence of action in the interior it is proved that air as well as heat is concerned. The familiar experiment in which iron-powder hanging to a magnet is heated in a bell-jar over water is next applied to prove that only a portion of the air disappears and this is followed by the passing of a measured volume of air through a tube containing heated copper, the residual gas being collected over water. Thus *nitrogen* is reached before oxygen. After the properties of nitrogen have been briefly studied, oxygen is obtained by heating mercuric oxide. This is introduced not by name, but as a red powder which bears the same relation to mercury as the black powder obtained by heating copper in the air does to copper. The student's knowledge of oxygen is then enlarged, with the aid of a cylinder of the compressed gas.

Other topics are handled similarly. It is plain that a student who studies chemistry in this manner will not only know something about it, but will also know *how* he knows it. He will have some idea of the way in which the science goes to work to get its subject-matter, which is at least as important to the student as that subject-matter itself. It is also clear that a subject handled in this way is taken up essentially in the historical order. This is more than a mere coincidence. As Goethe remarks, in his brief but exhaustive way, "Die Geschichte der Wissenschaft is die Wissenschaft selbst."

[4] "Leitfaden der Chemie," 5te aufl. (1910).

THE HANDLING, TRANSPORTATION, AND STORAGE OF PERISHABLE FOODSTUFFS.*

A Review of the Work of the Food Research Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.

(*Contribution from the Food Research Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.*)

BY

JOSEPH SAMUEL HEPBURN, A.M., M.S.

PART II.

The Scientific Study of the Handling of Perishable Foodstuffs.

COMMERCIAL METHODS 173—SCIENTIFIC INVESTIGATION OF COMMERCIAL METHODS IN THE FIELD 183—HARD FROZEN POULTRY 186—CHEMICAL CHANGES AND BACTERIAL GROWTH IN MILK AT LOW TEMPERATURES 186—STUDIES OF EGGS 189—CONCLUSION 191—BIBLIOGRAPHY 192.

COMMERCIAL METHODS.

The study of poultry handling has formed a large part of the work of this laboratory. The various commercial methods of dressing, transporting, storing, and marketing have been studied in the field and have been investigated in the laboratory, in order to learn which methods will produce a bird of the best quality for the consumer.

The eastern portion of the United States does not raise sufficient poultry to supply the demand of its own markets. By far the greater portion of the market poultry of the country is a product of the corn belt. The methods of breeding and feeding chickens have been studied in detail in the Eastern States, with a consequent increase in the quality of the eastern bird; in the corn belt, with its large farms, it has not been possible to study these particular branches of poultry husbandry, therefore in order to obtain a market product which will compete successfully in the eastern markets with fowls from nearby farms in respect

* Presented at the Stated Meeting of the Institute held Wednesday, May 17, 1911.

to quality, the western packers have been obliged to place great stress upon the killing, picking, chilling, packing, and transporting of chickens.

In the poultry belt chickens are prepared for market at packing houses. The birds may be taken directly from the farm to the slaughter house, or they may be submitted to a fattening process in a feeding station, then be removed to the packing house for slaughter. The killing of chickens is carried out in several ways. In bench killing the beak of the bird is fastened at the lower end of an inclined bench; in string killing the fowl

FIG. 1.

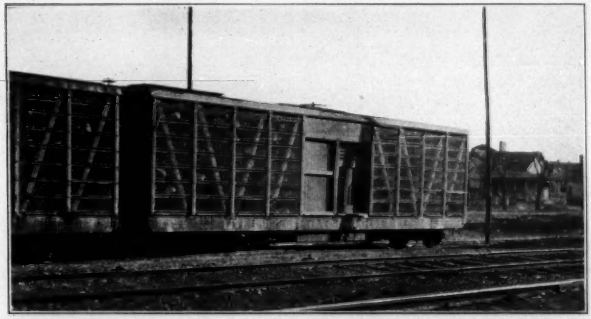
Arrival at the packing house of chickens from the farm.

is suspended by its legs by means of a rope; in either case the bird is killed by means of a knife-cut in the mouth. Other methods of killing exist, thus the bird may be held under the arm while administering the fatal cut, or the neck may be broken by mere muscular force. Since bad bleeding of a chicken leads to more rapid deterioration than occurs in a well-bled bird, an anatomical study has been made of the blood-vessels of the head and neck of the chicken, in order to devise a method of cutting which will insure proper bleeding. Two large veins run the whole length of the neck, one on each side, and are united by a diagonal "bridge vein" which is just below and behind the ear, and is farther front on the left side. This bridge vein lies just beneath the skin of the roof of the mouth and passes directly

across the U-shaped depression in the skull into which the upper part of the spinal column fits. By cutting the left neck vein and the bridge vein at their junction in the mouth of the chicken, good bleeding is insured. Moreover, the bones of the skull offer a backing to the knife and prevent it from sinking too deep, thus collection of blood in the soft tissues of the neck is prevented. It is interesting to note that at least thirty per cent. of the poultry coming to the New York market is incompletely bled.

The process employed for picking poultry varies. The birds may be scalded in order to loosen the feathers, then picked;

FIG. 2.



Railroad cars for transportation of live chickens.

since scalding is highly destructive to the structure of the skin, which serves as a protective coat to the carcass, a scalded chicken deteriorates rapidly. If the bird be dry picked, it is not only cut so as to bleed well, but the brain is pierced as well. The knife is run under the eye at such an angle that its point will touch the skull midway between the eyes and a little behind them; or the knife is placed half way down the groove in the roof of the chicken's mouth then thrust upward until it reaches the top of the skull midway between the eyes. The point of the knife is moved backward and forward slightly to destroy enough brain tissue to paralyze the bird, yet not kill it instantly. The resulting paralysis of the feather muscles facilitates dry picking. The rough picking may be done on the killing bench.

or may be carried out while the bird is suspended by its legs by means of a rope. For the final picking or "pinning" suspension by a rope may be utilized as in killing and rough dressing, or the workmen may hold the birds on their laps during the process. "String" killing, roughing and pinning form the better procedure. During picking, care should be taken to avoid rubbing or tearing the skin, and thus opening the way for bacterial invasion and loss in quality.

FIG. 3.

Interior of a feeding station—feeding pens.

The dressed poultry may be cooled in water and packed in cracked ice; or it may be cooled in air in an artificially refrigerated chill room, then packed dry. In the latter procedure, the birds are placed on movable racks and are subjected to a temperature of 35° to 40° F. (2° to 4° C.) in a chill room, which is provided with mechanical refrigeration, until the greater part of the animal heat has been removed, then they are transferred for the final chilling to a second chill room, the temperature of which is kept below 35° F. (2° C.), preferably at 30° F. (—1° C.). The packing should be done in the second chill room. The chickens are usually packed in small boxes, each of which

holds one dozen birds. Broiling chickens are packed with the breast up and the feet hidden, one dozen broilers form a layer and but one layer is placed in a box. Roasting chickens or fowls are laid on their side, six birds form a layer and two layers are placed in a box. The general tendency is to eliminate

FIG. 4.

Experimental shipment in a refrigerator car. In the background are the ice bunkers. The boxes on the left contain eggs. Two barrels are in the foreground; the one on the right, in which the contents cause the cover to protrude above the top of the barrel, contains ice-packed chickens; while the one in the centre, with the cover level with the top of the barrel, contains dry-packed chickens. The locked box, which rests on the latter barrel, contains a thermograph.

pressure on the tender tissues of the chicken as far as possible, therefore heads are wrapped in parchment paper and turned back so that they rest against the bony structure, rather than against the soft flesh of the thighs and breast; and the package is made smaller and smaller. Fowls are now sometimes packed a single layer to the box, and the carton for the single chicken or at most a pair of chickens is a recent advance which is

gaining in favor. If the boxes are held for several days before shipment from the packing house, they are kept in the chill room of lowest temperature or are placed in a "freezer" at a temperature of 0° to 15° F. (—18° to —9° C.), for from twenty-four to forty-eight hours. When not more than twelve chickens of ordinary size have been packed in a box, a period of forty-eight hours in a good freezer will very thoroughly harden the birds; a number of such boxes in a refrigerator car is a valuable aid in maintaining an equably cold temperature.

The boxes are always transported in refrigerator cars, so that the chickens may be kept at such a temperature for such a period of time, that they will reach the point of consumption in good condition after a railroad haul of one thousand miles or more. The bunkers of refrigerator cars, which are used for the transportation of dry packed poultry, are chilled by means of fine ice mixed with from 10 to 15 per cent. of salt. This mixture will maintain the temperature of the middle of the car, four feet from the floor, at 40° F. (4° C.) or under, provided the car be built with sufficient insulation and be in good order, *i.e.*, have tight-fitting doors, unbroken lining, etc. The boxes containing the most recently killed chickens are placed next the bunkers where the temperature frequently falls to 10° F. (—12° C.), and where the air about the top layer, 4 feet from the floor, often has a temperature not exceeding 30° F. (—1° C.). The boxes which have been in the freezer are packed together as tightly as possible in the central part of the car, and thus serve as a source of cold, where cold is most needed, *i.e.*, in the middle of the car, where refrigeration from the bunkers is least. The height of the load should not exceed four feet from the floor of the car. The cars are inspected and iced at icing stations during the railroad haul.

After poultry has been chilled or frozen the low temperature should be maintained constantly until the product is consumed, for a fluctuation in temperature is accompanied by a condensation of moisture, which creates a favorable environment for the action of bacteria and enzymes, and thus gives rise to decomposition. The wholesale dealer should keep dry packed poultry, between receipt and disbursement, in a mechanically refrigerated chill room at a temperature below 40° F. (4° C.). Frozen poultry should be carried in a room which is kept at a

temperature below 15° F. (—9° C.). The retail dealer usually keeps his stock of chickens in an ice-box, the temperature of which is about 45° F. (7° C.). However, even the retailers are beginning to use mechanical refrigeration, by means of which they may keep their poultry at a chill room temperature.

Water cooled chickens are always packed in barrels between layers of ice, and are kept in contact with ice until they reach the retail dealer. The barrels are usually transported in refrigerator cars. The retail dealer generally places his wet- (or ice-) packed chickens in a drained, zinc-lined box and mixes them with fine ice.

Air-chilling and dry packing would seem to offer a better mode of marketing than water-cooling and ice-packing. The latter process is uncleanly, places much pressure on the tender tissue of chicken muscle, and injures the skin, thus opening the way for bacterial invasion. Scientific research has proved the truth of these contentions. A bacteriological study has been made of the skins of chickens chilled in dry air, and in water and ice. After even a short keeping time, as market practices go, a markel preponderance of organisms was found in the skins of the birds which had been cooled in water and ice. The following data show that the acidity of the crude fat of chickens, which is a measure of decomposition, increases more rapidly in water-chilled, ice-packed chickens, than in air-chilled birds kept at 32° F., in dry air.

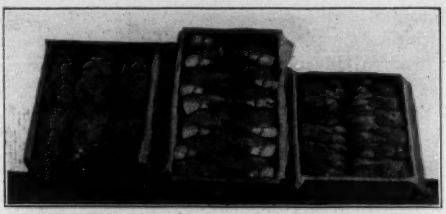
ACIDITY OF FAT AS AN INDEX OF FRESHNESS.

History of sample.	Acid value.
Broilers, air-chilled, 48 hours old	0.95
Same lot after 4 days, at 32° F.	2.10
Same lot after 12 days, at 32° F.	4.74
Fowl, air-chilled, 8 days at 32° F.	1.65
Same lot, 12 days, at 32° F.	2.41
Fowl, kept at 32° F. for 3 days	.80
Same lot, kept at 32° F. for 6 days	1.41
Broilers, water-chilled, ice-packed, 48 hours old	0.88
Same lot, 4 days in ice	4.57
Same lot, 7 days in ice	4.71
Fowl, water-chilled, ice-packed, 8 days	8.55
Same lot, 10 days in cracked ice	8.86
Fowl, kept in ice 3 days	2.20
Same lot, kept in ice 6 days	2.70

An extensive chemical and bacteriological study is now being made of the marketing of air-cooled, dry-packed chickens and of water-cooled, ice-packed birds.

Dry packed poultry may be either drawn or undrawn. If drawn, the drawing or evisceration may be "full drawn," "wire drawn" or "Boston drawn." In "full drawing" the body cavity is opened by a transverse cut across the abdomen and the vent is removed by cutting around it. The head is cut off and the intestines and viscera are completely removed. The heart, liver, cleaned gizzard and excess body fat are placed in the body cavity. The shanks and feet are removed and the

FIG. 5.



Dressed chickens packed in boxes, one layer to the box. On the left, roasters, six birds to a layer, packed on their sides. In the centre, broilers, twelve birds to a layer, "squatted" *i.e.*, packed with their backs up, and their heads and necks laid across the opposite birds. On the right, broilers, twelve birds to a layer, packed with their breasts up and their necks, heads and feet hidden.

hocks are thrust through the opening in the abdomen and the vent.

"'Wire' drawing consists in pulling out a loop of intestine by inserting the finger through the vent; cutting the loop, and drawing out the gut by careful traction until it breaks at the gizzard. The vent of a bird so drawn presents a normal appearance; the only indication of drawing is the collapsed abdomen.

"The 'Boston' drawing is a modification of the 'wire' in that a circular incision is made around the vent and the intestines pulled through until rupture occurs at the gizzard." The undrawn fowls are shipped with heads and feet on, and no incisions are made except for bleeding and braining.

Full drawn poultry decomposes the most rapidly during the interval between dressing in the packing house and final sale by the retailer in the city; Boston drawn and wire drawn birds

decompose less rapidly than the full drawn chickens, but more rapidly than the undrawn; the wire drawn birds usually suffer less decomposition than the Boston drawn. Undrawn poultry decomposes more slowly than that which has been entirely or partially eviscerated. These deductions are based on a study of the bacterial content of the wall of the abdominal cavity and on determinations of the acidity of the crude abdominal fat and of the quantity of loosely-bound or ammoniacal nitrogen present in the flesh.

Poultry may be held for weeks in a chill room or may be frozen solid and kept in that condition; in the former case

FIG. 6.

Pasteboard carton for two chickens with the lid removed. The wide border is formed of portions of four similar cartons with closed lids.

it is sold as "fresh," while in the latter case even if held for only a few weeks it is termed "storage." If a chicken be scalded or water-cooled, it will deteriorate rapidly even when hard frozen. If a bird be in the incipient stages of decomposition when hard frozen, deterioration will progress while in that state and decomposition will be rapid after thawing. Only dry picked, dry chilled poultry should be put into cold storage. Since the freezing should be rapid, the containers should be comparatively small, barrels should be avoided and boxes should be used. In order to exclude air from the birds, recourse is had to tight packages. Each chicken is wrapped in parchment paper when the stock is high grade; the result is two fold, the birds cannot rub against each other, and they cannot freeze into a solid mass. The packer usually ships poultry, which is to be stored, in a

refrigerator car to a cold storage warehouse; all possible precautions against bad treatment are taken. At the warehouse the boxes of poultry are kept in a room with mechanical refrigeration, at —10° F. (—23° C.) for several days, until the chickens are completely frozen. The boxes are then transferred to another room with a temperature of 10° F. (—12° C.) where they are kept until placed on the market.

Only poultry of good quality should be stored. If the chicken be poorly dressed, *e.g.*, scalded or water-cooled, or if it be in the early stages of decomposition, its quality will not be improved by its storage in the frozen state. In fact even the best of poultry is not improved by being kept frozen for any length of time. About the sixth month of carrying the sense of taste of a careful observer reveals a difference between frozen poultry and that freshly killed. However, up to nine months, the difference is so slight that it is of scarcely more than scientific interest. After nine months the flesh is undoubtedly wholesome and nutritious but a loss in flavor has occurred, proportionate to the period of storage.

It is highly desirable that frozen poultry be sold at retail in the frozen state, and that thawing occur in the ice box of the consumer. If the chicken be frozen by the packer, it should be allowed to "ripen" for several days in the ice box, or it will have a flat flavor. If the poultry has been several days in transit to the storage warehouse, and has been merely chilled prior to its arrival at that place, as soon as the bird has thawed in the ice box, it will be found to possess a good eating quality. Birds should not be thawed commercially by placing them in cold water, for such a procedure not only gives rise to rapid decomposition, but also removes a considerable portion of the flavor. Since the flavor is the first attribute of the fresh chicken to disappear during storage in the frozen state, care should be taken to retain the flavor in frozen birds, therefore thawing in water should be avoided. Thawing is best carried out by hanging the chickens in cool air, which is kept at the temperature of an ordinary ice refrigerator, the air should be circulated, to evaporate any moisture, which may settle upon any of the birds. Twenty-four hours should suffice for thawing a chicken of ordinary size, though a large roasting chicken may require a slightly longer period of time.

"So thawed, a bird well prepared and stored for a reasonable length of time—that is, from one season of production until the next as a maximum—will have a clear, fresh color in the skin, which will be soft in texture, slipping easily from the muscles beneath it. The flesh of breast and thighs may be very slightly deeper in color than in the fresh specimen, but so little that the change is negligible from a practical view-point. The fat is generally a little deeper in color and may have a slight taste and odor of rancidity."

After frozen poultry has been thawed and placed on the market, it should never be returned to the freezer. Refreezing is never a success, for loss in quality occurs after a second thawing. While the refreezing of poultry thawed in air is decidedly deleterious, that which is thawed in water and refrozen is in a much worse condition.

SCIENTIFIC STUDY OF COMMERCIAL METHODS IN THE FIELD.

In a scientific study of poultry handling, it is necessary to trace the history of a chicken from the time it arrives at the packing house until it finally reaches the consumer. The mode of killing, dressing and chilling must be known, a record must be kept of the transportation, and the bird must be followed through its stay—be it long or short—at the warehouse until it passes into the hands of the retail dealer, and then of the consumer.

A branch- or field-laboratory is installed in the packing house, so that a quantitative analysis, both chemical and bacteriological, may be made of the sample after the chilling process has ended and the birds are about to be packed. Visual "inspections" of such properties as odor, color of skin, etc., are made during the marketing as are also chemical and bacteriological analyses. It is impossible to express visual inspections in quantitative terms, and moreover such observations are influenced to a great extent by the personal equation of the observer. Chemical and bacteriological analyses are very delicate and accurate, are quantitative and are much less dependent upon personal equation.

A brief description of the research, upon the comparative rate of decomposition of undrawn poultry and that which had been drawn in various ways, will give an idea of the nature of the field work of this laboratory. Large mature hens were

killed by cutting the blood-vessels of the neck from within the mouth, and the brain was also punctured. They were well-bled, dry-picked, air-chilled; some were undrawn, others were eviscerated entirely or partially by the various methods of drawing (wire, Boston, full) which have been described in the preceding chapter. From their entrance to the chill room until their withdrawal from the retailer's for final analysis, the chickens were accompanied by a thermograph in order to obtain a complete record of the temperature. The birds were exposed for from twenty-four to forty-eight hours in a chill room which had a temperature between 27° and 41° F., with an average of 34° F. A sample was then analyzed; the other fowls were wrapped, boxed and placed in a refrigerator car, if a car lot was ready for shipment; otherwise they were held in a freezer at about 12° F. for three days on an average until a car was loaded.

The experimental packages formed part of an actual commercial shipment from the packing house. They were placed in the centre of the car, not more than four feet above the floor; the bunkers were filled with salt and ice, and instructions for icing en route accompanied the car. A period of seven and one-half days was usually required for the railroad haul of about 1700 miles. When the car arrived at its destination, the boxes were transferred to the chill room of the wholesale dealer, which had an average temperature of 32.6° F. The chickens were inspected and a sample taken for analysis. From the wholesaler the boxes were removed by wagon—a short haul—to the retail dealer. Since the equipment and methods of retailers vary within wide limits, arrangements were made for several of these dealers to participate in the research. They used the ice box for refrigeration. Whenever a display was made, the birds were hung in the shop window. The average temperature, including that of the window display, was 48° F. Inspections were made and samples removed for analysis when the retailer had sold at least one-half of his stock from the car lot of which the experimental packages had formed a part, and again "at the very last of the marketing or a little later than the retailer's regular sales, if the general market happened to be dragging." These samples, two from the retailer and one from the wholesaler, were submitted in this laboratory

to chemical and bacteriological analysis, including the determination of the acidity of the crude abdominal fat (as a measure of fat decomposition), the quantity of loosely-bound or ammoniacal nitrogen in the flesh (as a measure of protein decomposition), and the number of bacteria per gramme in the abdominal wall.

In these experiments all disturbing factors such as bad bleeding, had been eliminated. The birds differed only in mode of drawing; they had been subjected simultaneously to the same definite conditions of killing, picking, chilling, transportation and final marketing, therefore any differences between the chickens entirely or partially eviscerated and the undrawn birds, must be ascribed entirely to the method of drawing. A series of eleven shipments were included in this research which extended over a period of six months from January to June. From the average results of the analyses of the samples comprising these eleven experimental shipments, the following conclusions follow. Throughout the entire marketing period, the acidity of the crude abdominal fat increased progressively in all the samples, undrawn, wire, Boston and full drawn. The increase in acidity was greatest in the full drawn birds, in fact even in the packing house they had a slightly higher acid value than the other samples.

During the marketing, especially during the sojourn at the retail dealer's, the ammoniacal nitrogen in the flesh underwent a progressive increase, which was greatest in the full drawn chickens.

The number of bacteria in the abdominal wall also increased progressively. During the entire period, the undrawn birds contained the fewest and the full drawn the greatest number of organisms per gramme.

At the warehouse of the wholesale dealer or commission man, differences in quality due to mode of drawing were scarcely revealed by visual inspection. However, during the period of retail marketing, these differences became visible to a marked degree. Though stale, the last samples of undrawn chickens were still edible with a single exception; the wire drawn fowls were close to the undrawn; the Boston drawn birds were of a distinctly lower grade and occasionally were no longer edible. The full drawn chickens were always in the worst condition and frequently were no longer fit for food.

As already stated, the delicate and accurate methods of quantitative chemical and bacteriological analysis detect differences in quality due to mode of dressing even at the wholesaler's. These quantitative methods demonstrate that deterioration is progressive and is most rapid in the full drawn fowls and least rapid in the undrawn. The wire drawn and Boston drawn birds lie midway between the undrawn and full drawn; the wire drawn, which are more like the undrawn, are usually the better.

HARD FROZEN POULTRY.

The changes which occur in hard frozen poultry have already been mentioned in *Part I.* The flesh undergoes a desiccation with consequent increase in total solids and decrease in water content. The protein suffers a slow and specialized proteolysis, similar to that produced by the enzyme trypsin. The fat increases in acidity, and the saponification number and Hehner number change in the same direction simultaneously. The changes in the flesh, which are revealed by histological study, suggest an autodigestion. The bacteria which proliferate at 20° C., tend to increase. These changes, however, are chiefly of scientific interest. If a bird be given the proper treatment before, during and after storage in the frozen condition (as described in the chapter on Commercial Methods), it may be stored for a reasonable length of time, with the period from one season of production to the next as a maximum, without loss in food value.

CHEMICAL CHANGE AND BACTERIOLOGICAL GROWTH IN MILK AT LOW TEMPERATURES.

Milk has been kept at or a little below a temperature of 0° C. for periods ranging from a few days to almost two years. Under these conditions the casein undergoes a rapid digestion until finally more than fifty per cent. of it has changed to soluble compounds, and an increase in caseoses, amino acids and probably peptones occurs apparently at the cost of the digested casein. The proteolysis is pronounced at the end of two weeks, although it may vary in rapidity in different samples. The acidity of the milk increases at low temperatures and after several weeks is much higher than is required to produce a

TABLE I.

CHEMICAL CHANGES IN RAW MILK KEPT AT 0° C.

The Figures in Roman Represent the Per Cent. of the Various Forms of Nitrogen and the Per Cent. of Lactose in the Milk. The Figures in Italic Represent the Various Forms of Nitrogen as Per Cents. of the Total Nitrogen.

Period of keeping in days.	Distribution of the nitrogen.							Lactose.	Acidity c.c. $\frac{N}{10}$ NaOH per 100 c.c. of milk.
	Total nitrogen.	Casein nitrogen.	Albumin and syntonin nitrogen.	Caseose nitrogen.	Amino acid and ammonia nitrogen.	Difference between total nitrogen and sum of constituents determined.	Free ammonia nitrogen.		
Fresh	0.585	0.457 *78.12*	0.069 *11.79*	0.033 *5.64*	0.007 *1.20*	0.019 *3.25*	0.00047 *0.080*	5.3	18.0
7	0.571	0.432 *75.66*	0.084 *14.71*	0.018 *3.15*	0.018 *3.15*	0.019 *3.33*	0.00046 *0.080*	5.2	16.5
14	0.566	0.377 *66.61*	0.081 *14.31*	0.000 *0.00*	0.032 *5.65*	0.076 *13.43*	0.00000 *0.000*	3.8	32.7
21	0.569	0.335 *58.88*	0.069 *12.13*	0.167 *29.35*	0.033 *5.80*	*0.035 *6.15*	0.00075 *0.131*	3.7	30.7
28	0.537	0.295 *54.93*	0.053 *9.87*	0.161 *29.98*	0.022 *4.10*	0.006 *1.12*	0.00113 *0.210*	3.3	46.5
35	0.572	0.286 *50.00*	0.066 *11.54*	0.136 *23.78*	0.044 *7.69*	0.040 *6.99*	0.00040 *0.069*	3.5	56.0

* The sum of the nitrogenous constituents determined is greater than the per cent. of total nitrogen in this sample by 0.035 per cent.

curd spontaneously at ordinary temperatures; yet the phenomenon of curdling rarely occurred, in fact milk with an acidity as high as 101 c.c. of $\frac{N}{10}$ sodium hydroxide to 100 c.c. of milk did not form a curd even after exposure to the temperature of an ice box for days. A decrease in the lactose content also occurred. Table I shows the chemical changes undergone by a raw milk kept at 0° C. for 5 weeks, and analyzed when fresh and at intervals of one week thereafter.

Bacterial growth in milk stored at low temperatures was pronounced at the end of a week, even in the cleanest milk. The organisms always increased in number for five or six weeks and reached a maximum of hundreds of millions and occasionally of over a billion to the cubic centimetre. This enormous increase in bacterial content occurred in spite of the fact that the milk had been converted into a semi-solid mass of ice crystals by prolonged exposure to a temperature of 29° to 31° F. However neither odor nor taste indicated the presence of the enormous number of organisms, and the milk did not curd even on heating; in fact to the ordinary observer it was still suitable for household use, until the bacterial content began to decrease and the organisms of putrefaction made their presence known. Neutral organisms were present as well as those which form acid and those which act on protein. The liquifying organisms were more numerous and the acid forming bacteria were present in relatively smaller numbers than in milk kept at higher temperatures. "Certain species such as *B. formosus*, *B. solitarius*, and *B. Ravenel*, were especially resistant to cold and frequently were the predominating species, or almost in pure culture at the close of the experiment."

"A very marked difference in both the number and kind of organisms which developed on the plates was noticed, depending upon the temperature at which the plate was incubated. In certain experiments the maximum number grew at 37° C. In others the temperature at which the milk was stored served best for colony formation. The relative number of organisms growing at 37° C., 20° C., and 0° C., or a little below, varied greatly also with the length of time that the milk had been kept in storage, the organisms developing at body temperature being ordinarily greatly in excess at the beginning of the experiment

and diminishing until near its close, when a sharp rise was apt to take place."

When very fresh milk was kept in the laboratory at a temperature of 18° to 22° C., bacterial growth was rapid and profuse; the acid forming organisms were in high proportion and the liquifying organisms were relatively lower. The milk ordinarily curdled when the acidity had risen to between 23 c.c. and 28 c.c. of $\frac{N}{10}$ sodium hydroxide per 100 c.c. of milk. At this point only about one per cent. of the casein had been digested with the formation of soluble products.

STUDIES OF EGGS.

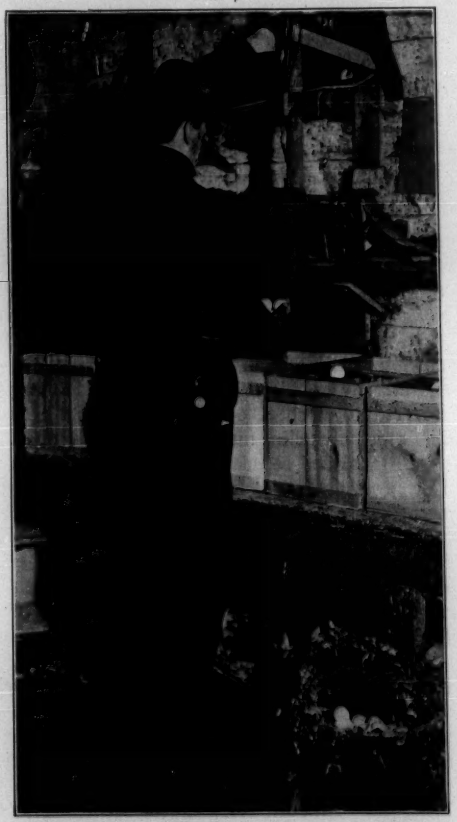
In the chemical study of eggs it became necessary to devise certain analytical methods. Thus the separation of white and yolk of raw eggs offered difficulties which were overcome in the following manner: the shell was broken, the white was poured off as completely as possible, and the yolk was washed free from white while still in the shell, by means of a gentle stream of water directed from a wash bottle. The yolk was then transferred to a sheet of filter paper and rolled about gently until dry; the vitelline membrane was not broken. White and yolk were analyzed separately, each became the object of a general or gross analysis. In addition the various forms of protein in the white were determined, and the fat in the yolk was extracted and studied. Since the fat could not be extracted directly from the liquid yolk by means of petroleum ether in a Soxhlet extractor, the yolk was first coagulated with alcohol, then extracted in the usual way. In like manner a technic was devised for the determination of the number and species of organisms in both the white and yolk.

An article upon the chemical composition and bacterial content of fresh eggs has already been published, and further studies of various phases of the egg industry are now in progress.

Fresh eggs of the Barred Plymouth Rock and White Leghorn breeds were studied separately. The eggs were laid by well-fed hens, the Plymouth Rock during September, October, and March; the Leghorn during February and March. "It is of interest to note that for these well-fed hens there is practically no difference in composition between Fall and Spring eggs."

Practically no difference in the chemical composition of the white was found between fresh Leghorn and Plymouth Rock

FIG. 7.



Candling eggs commercially in a packing house. The operator is holding the eggs before the view-holes of the electric egg-candle. The bucket at his feet is for the reception of "rots" and "spots." The scientific principles of this form of optical apparatus are discussed in Part I of this paper, JOURNAL OF THE FRANKLIN INSTITUTE, June 1911, clxxi, 593.

eggs. Although the gross composition or general analysis of the yolk was influenced but slightly by either breed or individual

samples, yet the yolk fat of both breeds was subject to wide variations in the values of the fat constants. Organisms were usually present in both white and yolk of these fresh eggs. "In the 57 experiments 18 had a decidedly greater number of bacteria in the yolk; 11 had the majority in the white and 21 had an almost even distribution; 7 were sterile." From 100 eggs, 36 species of bacteria, 3 varieties of molds and 2 varieties of yeast were isolated.

The commercial methods for the transportation and refrigeration of eggs have already been described in a previous publication of this laboratory.[1]

It is interesting to note that the chemistry of the egg received attention during the early days of American science. On May 19, 1794, John Redman Coxe presented to the Provost, the Trustees and Medical Faculty of the University of Pennsylvania, for the Degree of Doctor of Medicine, "An Inaugural Essay on Inflammation," in which he states, on page 30, that the experiments made by himself and others "prove that portion of air which we always find in one end of the egg to be oxygenous gas."[2]

CONCLUSION.

Modern science is showing a decided trend toward the conservation of natural resources—animal, vegetable and mineral—and of the public health. In this work of conservation, the various scientific bureaus of the Federal Government all have a part; the work of a few of these bureaus may be briefly reviewed. The Public Health and Marine Hospital Service of the Department of the Treasury guards the health of the nation. In the Department of the Interior several bureaus are engaged in conservation; the Reclamation Service carries out the work of irrigation; the Geological Survey studies mineral resources and water resources; and the Bureau of Mines has a two-fold function, the conservation of mineral wealth including fuels, and the conservation of life among mine workers, *i.e.*, the causes and methods of prevention of mine accidents. In the Department

[1] Pennington, *U. S. Department of Agriculture, Bureau of Chemistry, Circular No. 64*, 1910.

[2] The Library of the University of Pennsylvania contains a copy of Coxe's Essay, printed at Philadelphia by R. Aitken & Son, 1794.

of Agriculture the work of the Bureaus of Animal Industry, Forestry, Plant Industry, and Chemistry, among others, is in large part one of conservation. Thus the Bureau of Animal Industry carries out the meat inspection law, and stamps out contagious diseases of animals, such as the recent outbreak of hoof-and-mouth-disease in Pennsylvania and neighboring States. The Forest Service labors for the conservation of the timber supply. One phase of the work of the Bureau of Plant Industry is the study of the vegetable food supply. New vegetables are introduced; and methods of handling the vegetables and fruits already raised in this country are studied, so that they may pass from the producer to the consumer with least loss from decay or deterioration in quality during their journey. This work is illustrated by the investigation on the marketing of citrus fruits.

The Bureau of Chemistry enforces the Food and Drugs Act and carries out various investigations in the fields of bromatology and pharmacy, among which is the work of the Food Research Laboratory. The work of this laboratory has been described in the preceding pages. The course of perishable animal foodstuffs is followed from the producer to the consumer; during these studies the hearty co-operation is secured of packers, railroads, commission merchants, and retail dealers. The various problems which arise are solved by the application of the research methods of the physical sciences—chemistry and physics—and the medical sciences—physiological chemistry, bacteriology and histology. The various factors which influence the keeping qualities of perishable foodstuffs during their marketing are studied in detail; and methods are discovered which will improve the quality of the product as it reaches the consumer, and which will reduce the loss in marketing to a minimum. This is truly conservation of the nation's food supply!

BIBLIOGRAPHY.

The contributions from the Food Research Laboratory which have served, in large part, as the basis of Parts I and II fall into four divisions:

I.—Papers on Poultry. *Yearbook of the United States Department of Agriculture*, 1907, 197–206. *U. S. Department of Agriculture, Bureau of Chemistry, Bulletin No. 115*, 1908, 57–107. *Premier Congrès International du Froid, Rapports et Communications*, Paris, 1908, II, 216–260. *Journal of the American Chemical Society*, 1910, xxxii, 561–568, 568–572. *U. S. Depart-*

ment of Agriculture, Bureau of Chemistry, Circular No. 61, 1910; Circular No. 64, 1910; Circular No. 70, 1911. "The Keeping Quality of Poultry," by Pennington. Address made at the Annual Meeting Missouri Carlot Shippers of Eggs, Butter and Poultry, March, 1910. Published by the Association. Secretary's office, St. Louis.

II.—Papers on eggs. *Journal of Biological Chemistry*, 1910, vii, 109-132. *Seventh International Congress of Applied Chemistry*, London, 1909, *Section* vii. *Agricultural Chemistry*, 228.

III.—Paper on milk. *Journal of Biological Chemistry*, 1908, iv, 353-393.

IV.—Papers on fats. JOURNAL OF THE FRANKLIN INSTITUTE, 1909, clxviii, 365-384, 421-456; 1910, clxix 23-54. *Seventh International Congress of Applied Chemistry*, London, 1909, Section viiic. *Bromatology*, 268-271.

NOTE.—Part I, "The Function and Equipment of the Laboratory and a Résumé of the Researches Carried Out Therein," appeared in the JOURNAL OF THE FRANKLIN INSTITUTE, June, 1911, clxxi, 585-598. Part III, "Select Methods of Analysis" will appear in an early issue of the JOURNAL.

Gasolene Electric 'Bus for London. (*Amer. Mach.*, xxxiv, 785.)—A new type of motor bus is about to be introduced in London, of the combined gasolene-electric type. Two independent 12 horsepower, four-cylinder gasolene motors each drive, through an electric "dynomotor" and a flexible shaft, one of the rear wheels of the vehicle. When the load is light, the excess power of the engines is absorbed by the dynamotors, as dynamos, to charge a special 560 pound storage battery. When the load is heavy the dynamotors are automatically changed into electromotors, and assist the engines, taking power from the batteries. By this arrangement not only are the starting and control much smoother and quieter, but by the more constant load on the engines, the fuel economy is improved. The vehicles, including the wheels, are constructed of steel.

Magnolia Antifriction Metal. (*Amer. Machinist*, xxxiv, 798.)—According to the *Brass World*, the proportions used to make Magnolia metal are lead 80 pounds, antimony 15 pounds, and tin 5 pounds. The analysis shows lead 78.27 per cent., antimony 17.81 per cent., tin 3.88 per cent. and copper 0.04 per cent. The copper is present as an impurity.

Sulphur and Sulphuric Acid in the United States. (*Oil, Paint and Drug Rep.*, May 1, 1911.)—A report of the Geological Survey Department shows that the output of sulphur in the United States has risen from 3147 tons, valued at $88,100, in 1900, to 239,312 tons, valued at $4,432,066 in 1910. The United States still imports some sulphur, but exports about the same amount. A little comes in from Japan, but the business is not well established. A large

quantity of sulphuric acid is now made by the copper smelters, and in one case at any rate, the acid output in more profitable than the metal produced. The demand for sulphuric acid exceeds the supply from sulphurous ores and pyrites. In 1909 about 250,000 tons of pyrites were mined and nearly three times as much imported. There are large deposits of pyrites in New York, Virginia and California. The great sulphur deposits in Louisiana now yield immense quantities of commercially pure sulphur.

The Durability of Welded Steel Pipe. H. N. SPELLER. *Eng. News*, lxv, 347.)—Wrought iron pipe seems to have no advantage over steel as regards corrosion. It is believed there is as little occasion for corrosion in pipes and tools around boilers, and in hot water systems, as there is for smoke from a modern power plant. It is thought the problem will be solved by the removal of the oxygen dissolved in the water. The water is heated to a temperature high enough to expel all air, and then passed through an economizer, designed like a closed feed water heater, in which the excess of heat is absorbed by the cold feed on its way to the heater. A continuous supply of air-free water is thus obtained for service lines at any desired temperature.

Oil Fields of Japan. (*Petroleum*, vi, 829.)—According to an official Japanese publication, "Mining in Japan, Past and Present," the oil fields extend from the western coast of Sachalin in the north, through the western part of the central highlands of Hokkaido, and along the coast of the Sea of Japan, then traverse the provinces of Mutsu, Ugo, Utzen, Echigo, and Shinano, and reach the coast of the Pacific Ocean in the province of Totomi in the south. The annual output of crude petroleum has increased enormously in 20 years; in 1888 it was only 45,000 barrels and increased gradually to 1,727,300 barrels in 1907. Each barrel contains 42 gallons. This rapid development is chiefly due to the introduction of the American method of boring in 1890. The province of Echigo produces about 99 per cent. of the total output, and more than 90 per cent. of the Echigo output comes from the three oil-fields of Higashiyama, Nishiyama and Niitsu. Recently the oil industry has been concentrated among a few large companies and individuals. The oil deposits are found exclusively in the tertiary formation, and the strata consist of an upper layer of loam and clay, sandstone and conglomerates; a middle layer of sandy loam mixed with sandstone; and a lower layer consisting mostly of sandstone and clays, with tufa and sandstone at the bottom. The oil bearing strata consist of sandstone and tufa between layers of clay, and sometimes of clay only. The usual depth of the borings is from 600 to 1200 ft. The oil is transported from the wells to the refineries mainly by pipe lines, though some producers still use carts or boats.

FRANKLIN INSTITUTE

MEMBERSHIP NOTES.

NECROLOGY.

Mr. Francis Schumann, M.E., C.E., was born in Thuringia, Saxony, in 1844. He was the son of Carl F. W. Schumann, States Advocate and Professor of Jurisprudence in the University of Jena. The family moved to America in Mr. Schumann's childhood. He took up engineering and served throughout the Civil War as Topographical Engineer on Meade's staff. Later he became engineer to the Treasury Department at Washington, a position he held for some years. He then became manager of the Phoenix Iron Works at Trenton, N. J., which position he resigned to found the Tacony Iron and Metal Co., of which he was president and manager. He was engineer in charge of the construction of the City Hall tower, all the work for which, including the statue of Wm. Penn and the smaller groups were cast at Tacony. In addition many of the United States coastwise lighthouses were built under his direction. Mr. Schumann later became president of the Penna. Iron Works Co., a position he retained until his retirement.

He was past president of the Philadelphia Engineers Club, a charter member and first president of the American Foundrymen's Association, president the American Wire Glass Co., vice-president of the Tacony and Pelham Trust Companies. He was a member of the American Society Mechanical Engineers and of the Franklin Institute.

Mr. Schumann was well known as a writer upon engineering subjects, having written several books and a number of monographs, his "Heating and Ventilation" being still a standard work.

For the last five years of his life Mr. Schumann was an invalid. He leaves a widow and one son.

CORRESPONDENCE.

1600 HAMILTON ST., PHILA., June 22, 1911.

The Editor,

The Journal of the Franklin Institute,

Dear Sir:

In a review of "Recent Progress in Metallurgy," printed in the JOURNAL OF THE FRANKLIN INSTITUTE in November, 1906, I called attention to the novel utilization of blast-furnace slag by the United States Steel Corporation in the manufacture of true Portland cement in the following words, "Officials of the United States Steel Corporation are forming a number of subsidiary

concerns to the new Indiana Steel Company at Gary, Ind., which will become potent factors in the general operation of that new industrial centre when all is completed. One of the most significant and interesting of these, that has taken form, during the last week, is to be known as the Universal Portland Cement Company. It has a capital of $1,000,000 and its plans, while only vaguely outlined thus far, are understood to contemplate the manufacture of slag cement out of the furnace slag coming from the new blast furnaces to be built in the new town. . . . This will give the corporation a practical cement for all purposes with only the bare cost of making it. The saving will be enormous, as there is no investment for cement deposits, nor for much of the machinery that is necessary for the manufacture of the ordinary rock cement. The raw material is a pure waste, and passing through a process of extraordinarily short duration of time becomes a product of great commercial value. The plant is understood to be one of a number that will eventually be put up. Some may be built in Pittsburg, where they can take over the slag from the scores of blast furnaces of the corporation in this vicinity."

The foregoing information was credited to a then recent issue of *The Manufacturer* and further information was obtained from other sources in corroboration which may be found in the JOURNAL of November, 1906.

Prior to that time a certain quantity of slag cement called "Puzzolan" had been made and used for hydraulic work, or for setting under water, but this was entirely different in its properties from Portland cement.

Since the year 1906 the manufacture of Puzzolan has practically ceased while the production of Portland cement from blast-furnace slag has increased in a truly amazing manner. As evidence I enclose a paper which I think is worthy of being reprinted in the JOURNAL OF THE FRANKLIN INSTITUTE.

It will be observed that the first record of production of Portland cement made from a waste product (slag) of blast furnaces appearing in the table accompanying the paper was in the year 1900, when a total quantity of 32,443 barrels was made. In 1905 the production was 1,735,343 barrels, while in 1910 it had increased to 7,001,500 barrels. This was 1,349,234 barrels more than the total output of Portland cement in the United States in 1899! Remarkable indeed is this record, but still more so is the growth of the Portland cement industry from less than one million barrels in 1895 to more than seventy-three million barrels in 1910. The great increase in consumption has been accompanied by a correspondingly large reduction in cost of production, the reduction in cost causing the increase in consumption.

Had I ventured, in my address before the Metallurgical Section of the Institute in October, 1906, to predict that, in four years time, the production of the Universal Portland Cement Company from blast-furnace slag would exceed seven million barrels of Portland cement I would have been regarded as a dreamer.

Yours very truly,

ALEX. E. OUTERBRIDGE, JR.

THE UTILIZATION OF BLAST FURNACE WASTE.*

BY EDWARD M. HAGAR.

Until the last decade, practically the only utilization of the wastes or by-products of a blast furnace was the use of a portion of the waste gases to raise the temperature of the incoming blast through heating the brick-work in so-called hot stoves, and in some cases a small portion of the power value of the gases was obtained by burning them under boilers to generate steam for driving the blowing engines.

At the present time the calorific value of the waste gases is being utilized directly in gas engines for blowing purposes and for generation of electric power; a considerable portion of the slag is used in the manufacture of Portland cement, and the flue dust, consisting of the finest ore and coke particles, is being collected and converted so as to be rechargeable into the furnaces.

The aggregate saving or profits resulting from these three developments is a matter of millions of dollars per annum, and in a modern blast furnace plant, it would almost seem that pig-iron was the by-product; and, indeed, the investment in the equipment to utilize these former wastes, exceeds that of the blast furnace itself.

USE OF BLAST-FURNACE GAS.

The writer, in his work, has come in contact with these evolutions, with plants in operation, or under construction, of a capacity to produce 12,000,000 barrels of Portland cement per annum from slag and limestone, using over 1,300,000 tons of slag in a year, these plants being driven entirely by electric current generated by gas engines directly from the waste blast furnace gases, the power requirements being 40,000 horsepower for 24 hours every working day. In one of the cement plants the first commercial method for reclaiming the flue dust was discovered.

By using the blast furnace gases directly in combustion engines, after suitable washing to remove the grit, the power obtained from a given amount of gas is equal to at least two and one-half times that obtainable by burning the gas under boilers for generating steam for use in steam engines.

A modern blast furnace of the usual size, with gas blowing engines, and gas engines driving electric generators, will provide sufficient gas to furnish 7000 kilowatts electric power, in addition to driving its own blowing engines. This permits the most modern steel works, such as those at Gary, Ind., to practically do away with the use of coal for power purposes, operating the rolling mills by electric power from the surplus gases.

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*Presented before the Congress of Technology at the fiftieth anniversary of the granting of the charter of the Massachusetts Institute of Technology, and reprinted from *The Iron Trade Review*, June 22, 1911.

FLUE DUST.

The United States Steel Corporation, of which the Universal Portland Cement Co. is a subsidiary, has already installed 250,000 horsepower of gas burning and gas electric units, which, it can easily be figured, displaces or saves the consumption of approximately a million tons of coal per annum as compared to the old-fashioned methods.

With the modern high blast pressures, and the use of fine Mesabi ore, the finest of the particles, together with the coke dust, are blown out through the top of the furnaces and are caught in the flues, dust catchers and gas washers. The iron ore in this dust amounts to fully 3 per cent. of the total ore charged, which aggregates the large amount of approximately 1,250,000 tons per annum in this country. Until within a few years, this dust has been thrown away or used as filling, although containing about 40 per cent. metallic iron. For many years, efforts were made to use this material by compressing it into briquettes, but the cost of the operation, together with the fact that the briquettes disintegrated and the dust was again blown out, led to an abandonment of the briquetting plants.

The first commercially successful method of utilizing the dust was discovered by passing the material through the cement kilns of South Chicago. Experiments showed that with the proper heat treatment, the coke dust could be burned off and the iron ore conglomerated into nodules or nuggets averaging over 60 per cent. iron content. These nodules, when fed to the blast furnace, were easily and completely reduced. The fact that the sinter of the flue dust contains such a high percentage of iron and that all of the sinter is reduced, together with its physical shape assisting the steady movement of the charge downward in the blast furnace, thereby preventing so-called slips, makes the sinter more valuable per ton than any ore.

It was necessary to devise mechanical means for preventing the accumulation of the sinter in the walls of the kiln. Plants have been in operation for some years using this process, with endless chains carrying scrapers constantly passing forward through the kiln, and cooled in water on their return outside of the kiln. Recently other methods of utilizing dust have been devised which may prove successful commercially, and the indications are that within a short time the greater portion of this former waste will be prevented.

PORTLAND CEMENT INDUSTRY.

The development of the Portland cement industry in this country and the extension of its uses have been marvellous, and the accompanying table shows a remarkable increase in the production of Portland cement in the United States every year since 1895, when this country first reached the production of approximately 1,000,000 barrels.

It may be of interest to note the increasing percentage of the total American production shown by Universal Portland cement, which is the

only Portland cement manufactured in this country using slag as one of the raw materials. With the new plant now approaching completion the aggregate production of Universal Portland cement in the Chicago and Pittsburg districts will amount to over one-eighth of the country's total. Expressed in weight, the output of the finished product will be over 2,000,000 gross tons per annum. Our plants in the Chicago district will consume all the available slag that is suitable for the purpose from an aggregate of 19 blast furnaces in the South Chicago works of the Illinois Steel Co. and in the Gary works of the Indiana Steel Co.

Comparing the pig-iron production and Portland cement production of this country in figures of long tons, the percentage of Portland cement to pig-iron in 1890 was six-tenths of one per cent., in 1900 10.3 per cent. and in 1910 47 per cent. The continuation of any such relative growth would mean that before 1920 the tonnage of Portland cement would considerably exceed that of pig-iron. I would hesitate, however, to predict that such would be the case.

In this country Portland cement is manufactured from a number of raw materials, which, with a few exceptions, may be classed under four heads:

First—Argillaceous limestone (cement rock) and pure limestone.
Second—Clay or shale and limestone.
Third—Clay or shale and marl.
Fourth—Slag and limestone.

In the manufacture of Portland cement from slag and limestone, the molten slag flowing from the furnaces is granulated by a stream of water, loaded into cars and transported to the cement plants, where it is dried in rotary driers, and receives the first grinding; it is then mixed in automatic weighing machines, with the proper proportion of ground and dried calcite limestone. These are then ground together and burnt to a hard clinker at a temperature of nearly 3000 degrees Fahr., rotary kilns, using pulverized coal for fuel.

This clinker, after seasoning, is crushed and ground and mixed with a small percentage of gypsum to regulate the setting time. The cement is ground to such fineness that 96 per cent. passes through a sieve having 10,000 meshes, and 80 per cent. passes a sieve with 40,000 meshes to the square inch. It is then conveyed to the stock house for storage prior to shipment.

FURNACE FLUX.

It is necessary to use as a flux in furnaces supplying slag for cement manufacture, a pure calcite limestone. The limestone burnt with the slag must also be a pure calcite stone. It is also essential that the ores used be of a uniform and proper character.

Inasmuch as Lake Superior ores are noted for their remarkable uniformity of analysis, the resultant slag obtained from the use of these ores

and a pure calcite limestone, is more uniform in its analysis than any form of natural clay deposit used in the manufacture of Portland cement, and the variation in the proportions of the two raw materials used in the manufacture of Portland cement from slag is less than those of any other materials mentioned.

The rotary kiln commonly used ten years ago was 60 feet long and 6 feet in diameter. This has gradually been increased in length and diameter, until the modern kiln is 140 to 150 feet long and 8 to 10 feet in diameter, and there are a few even larger kilns in use. Kilns are usually set at an incline of three-quarters of an inch to the foot. With the lining and contents the modern kiln weighs 150 tons, and in revolving upon two bearings presents interesting constructional features.

BUFFINGTON PLANT.

In the case of the plant at Buffington, Ind., using 26,000 horsepower, situated between South Chicago and Gary, Ind., electric power is supplied at 22,000 volts from the steel works at these points. Each piece of machinery is driven by its individual motor, supplied with alternating current at 440 volts. The high tension line is connected through the cement plants, and the gas engines at these two steel works, 14 miles apart, operate continually in parallel. This enables the cement plant to draw its power from either source, or from both sources at the same time, as may be desirable. It has happened that one of these works has supplied power to operate the cement plant and furnished additional power at the same time to the steel works at the other end of the line.

True Portland cement in which slag is used as one of the raw materials, should not be confused with Puzzolan or so-called *slag cements*, which are simply mechanical mixtures of slag and slaked lime ground together without burning. Such cements are suitable only for use underground and in moist locations. The manufacture of Puzzolan cements in this country has practically been abandoned.

The remarkable growth of the Portland cement industry is not equalled by any other manufactured article. This is due to the economy, durability, and plasticity of cement and concrete work. While large engineering work, such as dams, bridges, and heavy reinforced concrete buildings, consume large quantities of cement, the bulk of consumption at the present day is in a multitude of small uses. It takes an average shipment of only five barrels a day to take care of the average customer of a large cement company. For example, there is a steady increase in the application of cement to new uses on the farm, such as silos, fence posts, barn floors, feeding floors, watering troughs, corn cribs, etc. There, as elsewhere, concrete is rapidly displacing all forms of wood construction, this process being hastened by the continually advancing cost of lumber.

CEMENT PRODUCTION OF THE UNITED STATES.

Year.	Production of Portland cement of United States, barrels.	Production of Universal Portland cement, barrels.	Percentage of Universal to total American production of Portland cement.
1895	990,324	.....	....
1896	1,543,023	.....	....
1897	2,677,775	.....	....
1898	3,692,284	.....	....
1899	5,652,266	.....	....
1900	8,482,020	32,443	0.39
1901	12,711,225	164,316	1.29
1902	17,230,644	318,710	1.85
1903	22,342,973	462,930	2.08
1904	26,505,881	473,294	1.78
1905	35,264,812	1,735,343	4.92
1906	46,463,424	2,076,000	4.55
1907	48,785,390	2,129,000	4.36
1908	51,072,612	4,535,000	8.89
1909	62,508,461	5,786,000	9.27
1910	73,500,000*	7,001,500	9.52

* Government estimate.

BOOK NOTICE.

LEÇONS SUR L'ÉLECTRICITÉ, Professées a l'Institut Électrotechnique Montefiore. Par Éric Gerard, Directeur de cet Institut. Eighth edition, entirely reset. two volumes, paper covers. Vol. I.—Elements of Electricity and Magnetism, Electrometry, Theory and Construction of Electric Generators, xii, 975 pages, 9½ x 6½ inches with 458 figures. Price 12 francs. Vol. II.—Transformers, Transmission Lines and the Distribution of Electrical Energy. Applications to telegraphy and telephony, to lighting, to the production and transmission of motive power, to traction, to metallurgy and to industrial chemistry. 990 pages, 9½ x 6½ inches with 489 figures. Price 12 Francs. Gauthier-Villars, Paris, 1910.

The distinguished author of this voluminous treatise needs no introduction to American readers, an early edition having been translated into English in 1897. Since that time, it is evident that the growth of the work has not suffered from neglect in keeping abreast with the constantly increasing scope and elaboration of the subject. Covering the entire field of electrical engineering, that the work is not even more voluminous speaks highly for the discrimination shown in treating the component topics.

The work combines the desirable qualities of the analytic method of the physicist with the material procedure of the engineer. Fundamentals are treated at length and, without attempting to exhaust any one particular department, each is treated with a degree of thoroughness only excelled in special monographs. As is already well known the author's presentation is at once precise and lucid and even the student who knows only "college" French, will find profit in keeping it readily accessible.

PUBLICATIONS RECEIVED.

Handbook for Iron Founders issued by the Frodair Iron and Steel Company, Limited. 155 pages, 16mo, cloth. London, Company, no date.

Improved Cast Iron, How to Get it in the Foundry. Lecture Delivered to the British Foundrymen's Association (Scottish branch) at Glasgow, on December 10, 1910, by John F. P. Lewis (of the Frodair Iron and Steel Co., Ltd.) 15 pages, 12mo. London, Oliver & Co., no date.

A Systematic Handbook of Volumetric Analysis; or the Quantitative Determination of Chemical Substances by Measure, Applied to Liquids, Solids and Gases. By Francis Sutton, F.I.C., F.C.S. 10th edition, revised throughout with numerous additions, by W. Lincolne Sutton, F.I.C., and Alfred E. Johnson, B.Sc. 621 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Co., 1911. Price $5.50.

Recherche pratique et exploitation des mines d'or. Par Georges Proust, ingenieur civil. 110 Pages, illustrations, 12mo. Paris, Gauthier-Villars, 1911. Price, in paper, 2 francs, 75 centimes.

Elektrochemische Umformer (galvanische Elemente). Von Johannes Zacharias, ingenieur. 262 pages, illustrations, 12mo. Wien, A. Hartleben's verlag, 1911. Price, in paper, 4 marks.

Les Lampes Électriques. Par H. Pécheux, docteur ès sciences. 186 pages, illustrations, 12mo. Paris, Gauthier-Villars, no date. Price, in paper, 50 cents.

U. S. Bureau of Mines, Bulletin 12. Apparatus and Methods for the Sampling and Analysis of Furnace Gases. By J. C. W. Frazer and E. J. Hoffman. 22 pages, illustrations, 8vo. Washington, Government Printing Office, 1911.

U. S. Bureau of Mines, Bulletin 14. Briquetting Tests of Lignite at Pittsburg, Pa., 1908–9—with a chapter on sulphite pitch binder. By Charles L. Wright. 64 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1911.

U. S. Coast and Geodetic Survey. Results of Observations Made at the Coast and Geodetic Survey Magnetic Observatory near Honolulu, Hawaii, 1907 and 1908. By Daniel L. Hazard, Computer, Division of Terrestrial Magnetism. 95 pages, plates, quarto. Washington, Government Printing Office, 1911.

Tobin Bronze. Descriptive pamphlet. The Ansonia Brass and Copper Company. 35 pages, illustrations, 16mo. Ansonia, Conn. October, 1908.

U. S. Department of Agriculture, Office of Public Roads, Circular No. 94. Progress reports of experiments in dust prevention and road preservation, 1910. 56 pages, 8vo. Washington, Government Printing Office, 1911.

U. S. Department of Agriculture, Forest Service, Bulletin 88. Properties and Uses of Douglas Fir. Part 1, Mechanical Properties. Part 2, Commercial Uses. By McGarvey Cline, Director, Forest Products Laboratory, and J. B. Knapp, Assistant District Forester. 75 pages, illustrations, plates, map, 8vo. Washington, Government Printing Office, 1911.

CURRENT TOPICS

The Cause of Internal Corrosion of Hot Water Pipes. M. J. FALKENBURG. (*Eng. News*, lxv, 347.)—The return pipes in the heating system of a modern office building corroded seriously with a few months service. Apparently the cause was traced to the presence of zinc, and probably the black iron return pipes were manufactured from billets to which scrap metal containing zinc had been added, and the mass heated only hot enough to roll and not enough to volatilize the zinc. The scale on the corroded pipes contained 0.3 per cent. zinc, the condensed water near a corroded place contained zinc oxide and carbonate, and the original pipe between 0.2 and 0.4 per cent. zinc. There was no zinc in the steam risers, which showed no corrosion; and there was no evidence of serious corrosion in the pipes of another building heated from the same source.

Chemical Action Induced by Cathode Rays and Canal Rays. E. P. PERMAN. (*Chem. Soc. Proc.*, xxvii, 94.)—The transmutation of copper, thorium, and uranium by means of cathode rays and canal rays has been attempted and the chemical effect of canal rays has been studied. The conclusions are: (*a*) Neither cathode nor canal rays cause any transmutation of elements. (*b*) Canal rays in air or oxygen have a strong oxidizing action. (*c*) The oxidizing action appears to be mostly direct, but is accompanied by a scattering effect. (*d*) Many substances are decomposed by the action of canal rays independently of the nature of the gas in which the rays are produced.

Flaming Arcs. EDIT. (*Elec. Rev. West. Elec.*, lviii, 322.)—The slow progress in the adoption of this type of illuminant is probably due to the "inertia" of purchasers. It should be used extensively on account of its high operating efficiency, the agreeable color of the light, the large area of the source, and its even distribution. Flaming arcs should always be mounted at least 20 feet from the ground, and often better results are obtained when as high as 40 feet. The power of penetration possessed by flaming arc rays makes them valuable in shops where there are clouds of vapor obscuring the light.

Platinum, the Most Precious Metal. ANON. (*Electrical Rev.*, lviii, 579.)—Platinum is becoming scarce. Its chief source is the Ural Mountains of Russia. About one per cent. of the total supply is found in the United States and small quantities in Canada and

Columbia. Recent prices are $43 per oz. for hard metal and $41 per oz. for soft metal. This is rather more than twice the price of gold, which is $20.67 per oz.

Preventing Corrosion of Metals by Electricity. ANON. (*Elect. Rev. West. Electr.*, lviii, 326.)—According to a recent Australian invention, the galvanic action of corrosive substances in water may be neutralized by sending weak electric currents to the metals to be protected. Tests made at Melbourne University on metals immersed singly and in connected pairs in hot and cold sea water, and in dilute acids, showed that all destructive galvanic action was suspended by a small expenditure of electric power.

Cost of Water Waste. ANON. (*Eng. Record*, lxiii, 374.)—Most people do not recognize that, at New York City water rates, the small drip of a leaky faucet wastes annually from $2 to $6 worth of water; or that the cost of a leak flowing from an orifice 1/32 inch in diameter, under a pressure of 39 lbs. will amount to $11 or $12 annually on a meter rate basis. Hence it is necessary to correct the idea that a small leak is too insignificant to warrant attention.

Packing Machinery for Export. F. H. DAVIES. (*Amer. Mach.*, xxxiv, 927.)—The careful packing of machinery for export is very essential in securing export business. Goods should be packed so as to be able to withstand careless and rough handling, to keep out moisture, to resist the attacks of insects and vermin. Yet care should be taken that it is no heavier than is necessary. All marking should be in simple language and in plain letters and figures. This article will be found worthy of close attention by exporters.

Safety of Oil as Liquid Fuel. (*Amer. Mach.*, xxxiv, 890.)—It has been shown that oil with a flash-point of 239°F. will not ignite if fired into with a shell, and if dynamite is exploded in a reservoir of this oil, it only throws up jets of oil which do not ignite. The only dangerous liquid fuel oils are those which have not parted with their volatile, inflammable gases; such as absolutely crude oils. In all ordinary, commercial, fuel oils, these portions are removed, and the oil is safe and contains no power of spontaneous combustion. Oil with a fire-test of 180° to 200° F. is as safe as coal, and it will not ignite when stirred with a red-hot poker, nor when hot coals are thrown in it.

A New Highly Active Radium Preparation. A. FISCHER. (*Pharm. Post.*, xliv, 193.)—At the Neulengbach radium works, a crude radium sulphate is obtained directly by a combined extraction process; the acid and alkaline fusion. Ten thousand kilos of pitchblende residues can be treated in this way, and crude radium chlor-

ide obtained in 6 weeks, and low grade ores, containing 3, 6, 10 to 15 per cent. of uranium oxide, which cannot be treated by the Curie-Debierne process, are available for radium manufacture. Experiments on living skin showed that radium emanation enters the organism mainly by inhalation. The Neulengbach works furnishes preparations which in sterile sodium chloride solutions exhibit activities up to 300,000 Mache units.

Temperature Measurements in an Experimental Carborundum Furnace. H. W. GILLETT. (*J. of Phys. Chem.*, xv, 213.)—This is an extensive inquiry into the forms of pyrometer which may be used for the accurate determination of temperatures from 1700°–2500°C. in a carborundum furnace. Three instruments were used: (1) a Wanner pyrometer, specially sensitized; (2) a Morse Thermoguage (Holborn-Kurlbaum pyrometer) with improved calibration; and (3) a specially improved form of Thwing radiation pyrometer; all these being calibrated against a spectrophotometer. Working with the three pyrometers, the temperature of the formation of siloxicon was found to be 1540°C.±30° C., that of carborundum 1820° C. ± 20° C., and the decomposition temperature of carborundum was 2220° C. ± 20° C.

Explosions of Compressed Air. W. L. SAUNDERS. (*Eng. and Mining J.*, xci, 713.)—Compressed air may easily become charged with inflammable vapors, through using in the compressors lubricants with too low a flash-point; or if the pipe lines are not regularly drained at low points, where oil, etc., is liable to accummulate. Cases have occurred where pipe lines have been shattered through the ignition of such accummulations of inflammable vapor, probably by heating due to compression. For this reason the use of kerosene to clean air pipes is condemned. These accidents can be avoided by regular inspection of the interior of the compressors and of the whole system of compressed air.

Automobile and Gas-Engine Lubricating Oils. F. SCHWARZ AND H. SCHLÜTER. (*Chem. Zeit.*, xxxv, 413.)—Several oils, some of which had proved suitable and others unsuitable in practice, were examined for their density, viscosity and flash-point, but these determinations gave no indication as to their suitability. In the case of cylinder oils, which must not leave a residue in the cylinder and should not give an objectionable odor to the exhaust, it was found that extraction with acetone at the ordinary temperature removed the noxious constituents of the oil. From 66 to 93 per cent. of the oil was insoluble in acetone, and had a higher flash-point and ignition-point and a lower density and viscosity at 20° C. than the original oil. Hence the proportion insoluble in acetone is a rough measure of the suitability of a cylinder oil.

Change of Structure of Aluminum. H. LE CHATELIER (*Comptes rend.*, cli, 650.)—Some aluminum articles underwent spontaneous disintegration, and on examination showed that in each case a cellular structure had developed, and that the disintegration was evidently due to the opening of the joints between the cells. Laboratory experiments indicated that the presence of small quantities of calcium were probably the cause of the development of this cellular structure.

Anticorrosive Alloy. G. JACQUIER, Johannesburg. *Eng. Pat.*, 20601 of 1910.—This anticorrosive alloy has the composition aluminum 92 per cent., bismuth 2, copper 5 and silicon 1 per cent.; or of aluminum 91 per cent., bismuth 2, copper 5 and magnesium 2 per cent. The metals except the aluminum are melted together, and then the molten aluminum added.

Coffee Glazes Containing Arsenic. F. E. NOTTBOHM AND E. KOCH. (*Z. Unters. Nahr. Genussm.*, xxi, 288.)—Shellac is one of substances used for glazing coffee beans, and attention is drawn to the fact that shellac is sometimes colored by arsenic trisulphide. Samples of shellacs were found to contain from 0.0785 to 0.12 per cent. of arsenic, while samples of colophony were free from arsenic. Coffee beans glazed with arsenical shellac were found to be strongly contaminated with arsenic.

Two New Compounds of Stannous Chloride and Ammonia. A. J. SOFIANOPOULOS. (*Comptes rend.*, clii, 865.)—Persoz found that stannous chloride, heated with dry ammonia gas, gave a compound with the formula $SnCl_2NH_3$. The author finds that this compound is produced in the cold, even below 0° C. A compound with the formula $SnCl_2.2NH_3$ is formed by passing dry, cooled ammonia gas over a shallow layer of well dried stannous chloride in a large glass tube, cooled by a mixture of ice and salt. Ammonia is passed until the contents of the tube are of a uniform light yellow color. This product should be kept in a colored bottle, shaded from light. A third compound, $3SnCl_2.2NH_3$, is formed by the action of gaseous ammonia on stannous chloride at a temperature between 120° C. and 300° C. It is a reddish-brown crystalline mass, powerfully double-refractive, and is apparently the most stable of the ammonia and stannous chloride compounds.

Colored Etching of Steels. F. ROBIN AND P. GARTNER. (*Rev. Mét.*, viii, 224.)—The polished specimens are etched in a saturated solution of picric acid for thirty seconds, and it is claimed that on rinsing them in water and then allowing them to dry without wiping, a variety of colors are produced, by which the various constituents, such as austenite and martensite, may be distinguished. The original article is illustrated with microphotographs.

Spectrum of an Electrically Heated Carbon Rod. M. LA ROSA. (*Ann. Physik.*, xxxiv, 222.)—When a carbon rod of 2 or 3 mm. diameter is heated white hot by a current of 15–18 ampères per square mm. passed through it, it is surrounded by a layer of incandescent gases, the spectrum of which was investigated. It consists of a faint continuous background on which a number of bands or lines are seen. The bands are those of the Swan spectrum, with faint traces of the so-called cyanogen spectrum, while the lines are those of the metallic impurities found in the carbon. When the rod is heated in pure nitrogen (after all occluded gases are removed) no metallic lines appeared, and scarcely any trace of the cyanogen bands, while those of the Swan spectrum (presumably due to carbon vapor) were seen better than when the rod was heated in air. This, and similar experiments, show that oxygen is necessary for the appearance of the metallic lines. The explanation suggested is that in the hot carbon rod the metallic impurities form carbides, which are broken up only by oxygen, thus leaving the metal free to radiate.

The Use of Storage Batteries for Electroplating. G. M. HOWARD. (*Brass World*, vii, 89.)—Due to its steady high voltage the lead battery is particularly well suited for plating work, and is superior to low voltage dynamos. Storage batteries may be used as a regulator for a dynamo. As auxiliaries they are superior, two batteries being alternately charged and discharged. Systematic attention is necessary for storage batteries. The principles of the operation are summarized.

Nitrification by the Ultra-Violet Rays. D. BERTHELOT AND H. GAUDECHON. (*Compte rend.*, clii, 522.)—An aqueous solution of ammonia, after being exposed for a few hours to the action of ultra-violet rays in the presence of oxygen, gave all the reactions for nitrites. The oxidation appears to be arrested at the nitrite stage, for no nitrates were detected. The same result occurs when air is substituted for oxygen. The production of nitrites was observed in solutions of ammonium carbonate, ammonium chloride and ammonium sulphate under similar conditions, but much more slowly in the two latter cases where the amount of hydrolysis is small. Solutions of urea and several primary and secondary amines are decomposed with the liberation of ammonia. Nitrates exposed to the rays are degraded to nitrites. A solution of ammonium nitrate gives nitrite with evolution of nitrogen and oxygen, showing that the nitrite is produced both by oxidation of the ammonium group and the deoxidation of the N_2O_6 group. The formation of nitrites is also detected in solutions of potassium nitrate. There are many points of resemblance between the action of these ultra-violet rays and that of certain micro-organisms.

The Melting of Carbon by the Joule Effect. M. LA ROSA. (*Ann. Physik.*, xxxiv, 95.)—Moissan concluded that carbon cannot be melted except at high pressures. The author made experiments which indicate that at least incipient fusion can be attained. Heavy electric currents up to 90 ampères were passed through small carbon rods of 1 to 3 mm. in diameter. If the current was increased at once to the highest amount, the rod usually exploded violently, partly on account of the liberation of occluded gases, and partly on account of the sudden expansion of the rod. When the current was applied more slowly, the rod sometimes bent under its own weight. From this effect and from the appearance of the particles of the exploded rods, the conclusion is reached that carbon has partially melted. Since especially purified carbon, containing less than 0.08 ash was used, it is considered that the fused appearance of the rods could not have been due to the presence of impurities.

The Formation Temperature of Carborundum. H. W. GILLETTE. (*J. Ind. Eng. Chem.*, iii, 242.)—The decomposition point of silicon carbide into graphite is found to be 2220° C. ± 20° C.; the formation of crystalline silicon carbide occurs at 1820° C. ± 20° C., and the formation of siloxicon at 1540° C. ± 30° C. A description of his furnaces and of the apparatus for measuring the temperature is given.

On the Duration of the Phosphorescence of Uranous Salts. J. BECQUEREL. (*Mon. Scient.*, lxxiv, 347.)—It is known that the duration of phosphorescent light is longer as the temperature is lower. Lenard has shown that three phases can be recognized; the hot phase, in which the emission is proportional to the excitation (fluorescence); the permanent phase, when the emission is prolonged after excitation; the cold phase, which is a storing up of the luminous energy, without any emissions. The three phases change gradually from one to the other. Certain uranous salts show a remarkable property; even at the extremely low temperature of the solidification of hydrogen (—259° or 14° absolute) they show hardly any other phase than the hot phase. The examination in the phosphoroscope of uranous salts cooled in liquid nitrogen (—193°) and then held at the ordinary temperature, gives the following results. A certain number of salts, principally organic, acetates, tartrates, oxalates, follow the general law; at a low temperature they have a notably longer phosphorescence than at the ordinary temperature; at —193° some even remain luminous for several seconds after removal from the tube of the phosphoroscope. On the other hand the uranous sulphates and the nitrate show no change in the duration of the emission. Different properties of the uranous salts lead us to think that the mechanism of phosphorescence can be localized in the radical uranyl, UO_2. In spite of the variability shown by certain salts, the constancy of the duration of the phos-

phorescence in the other compounds, is quite in accord with this hypothesis. It remains to be shown if this phenomenon persists with the same stability at the lowest temperatures obtainable.

The Expansion and Physical Condition of Water. J. DUCLAUX (*Journal de Physique*, Feb., 1911.)—A large number of empirical formulas have been proposed to represent the expansion of water, for a given interval of temperature. Most of them are either very complicated, or are only exact between very circumscribed limits of temperature. Duclaux presents a formula which agrees with the experimental data for a long interval, from —10° C. to + 150° C., and has besides a simple theoretical significance. According to Röntgen, at ordinary temperatures, water may be considered as a solution of ice, that is to say, that it contains polymerized molecules, probably identical with those of the solid ice. These polymerized molecules are lighter than water, and the volume of liquid is increased by their formation. The lower the temperature the more numerous they become. The maximum density of water is well explained by this hypothesis: when water is cooled below 4° C., the non-polymerized molecules contract. But on the other hand the number of polymerized molecules increases. It is easily conceived that the resultant of these two opposing forces can cause an increase in volume. Duclaux's proposed formula comprises two terms; the first of the parabolic type, $a + bt + ct^2 + \ldots$, would represent the expansion of a liquid constituted solely of simple molecules. The second term takes into account the expansion of volume due to polymerization; it is almost proportional to the number of molecules of ice, and is well expressed by

$$K.\ 10^{\frac{n}{T}}$$

where K and n are constants and T is the absolute temperature. This becomes then

$$v = a + bt + ct^2 + K.\ 10^{\frac{n}{T}}.$$

This formula agrees with experimental results, when suitable values are given to the constants. The measurements of Thiesen, Scheel, and Diesselhorst, are very accurately represented, when

$$\begin{array}{ll} a = 0.991833, & 10^6 c = 2.84475, \\ 10^4 b = 2.25208, & 10^6 k = 0.53977, \end{array} \qquad n = 1143$$

Further, the theoretical reasons which lead to a formula of this type for water, are equally applicable to all liquids with linked molecules (alcohols, organic acids, and probably mercury at low temperatures). It is probable then that the expansion of liquids can be best represented by analogous expressions.

The Presence of Zinc Nitride in Zinc Powder and in the Zinc of Commerce. C. MATIGNON. (*Comptes rend.*, clii, 1309.)—Briegleb and Geuther have shown that zinc heated to low redness in a current of nitrogen, becomes covered with a gray powder, which prevents the agglomeration of the metallic filings even when raised above their fusion point. Zinc covered with this gray powder disengages a little ammonia when fused with potassium hydroxide. It has been observed that zinc fixes nitrogen most rapidly at about 600° C., under these conditions zinc containing nearly 10.6 per cent. of nitrogen has been obtained. It is certain that in the majority of cases the quantity of nitrogen contained in 1 k.g. of commercial zinc does not exceed 30 to 40 mg. Zinc nitride seems to exist in all commercial zinc powders; it is also found in some zincs, but in extremely small quantity. Zinc white (oxide) does not contain any.

The Clancy Cyanide Process. ANON. (*Eng. Mining Jour.*, xci, 904.—This is the practical application of the process as now installed at the Ajax mill, near Victor, Col. It is conducted in two stages: (1) The generation of a cyanogen halide, usually cyanogen iodide, which attacks the sulpho-telluride minerals, dissolving them with the gold; (2) the regeneration of the cyanogen by the reaction between calcium cyanimide and the thiocyanates and alkali cyanates. The apparatus consists of the usual fine grinding and cyanogen equipment, a low voltage direct current generator, a cyanimide solution tank, and an electrolyzing apparatus which is hung in the agitating tanks in use. The anodes are of fused magnetite and are hung in pairs between the cathode sheets which consist of iron plates. The surface area of each anode is 2.2 square feet. The anode is closed at the lower end, and the upper end is cemented into a porcelain cap, which insulates the anodes from the frame and protects the copper connections from the solution. The cathode is insulated in a similar manner. The current density varies, being generally about 18 ampères per square foot of anode surface. The difference of potential is about 7 volts and a current of about 50 ampères is passed through each anode.

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